

## Chapter 2

### Flame Atomic Absorption and Emission Spectrometry

#### 2.1 Introduction and History of AAS

The first observation of atomic emission dates back to at least the first campfire where hominoids/humans observed a yellow color in the flame. This color was caused by the relaxation of the 3p electron to a 3s orbital in sodium (refer to the energy level diagram in Figure 1-3 given earlier), and in part by carbene ions. Slightly more advanced, but still unexplained observations were responsible for the first development of colorful fireworks in China over 2000 years ago. A few of the more relevant discoveries for atomic spectroscopy were the first observations by Newton of the separation of white light into different colors by a prism in 1740, the development of the first spectroscope (a device for studying small concentrations of elements) in 1859 by Kirchhoff and Bunsen, and the first quantitative analysis (of sodium) by flame emission by Champion, Pellet, and Grenier in 1873. The birth of atomic spectrometry began with the first patent of atomic absorption spectrometry by Walsh in 1955. In the same year, flames were employed to atomize and excite atoms of several elements. The first atomic absorption instrument was made commercially available in 1962. Since then, there have been a series of rapid developments that are ongoing in atomic and emission spectrometry including a variety of fuels and oxidants that can be used for the flame, the replacement of prisms with grating monochromators, a variety of novel sample introduction techniques (hydride, graphite furnace, cold vapor, and glow discharge), advances in electronics (especially microprocessors to control the instrument and for the collection and processing of data), and the development of atomic fluorescence spectrometry. Surprisingly, detection limits for the basic instruments used in flame atomic absorption and emission spectrometry have improved little since the 1960s but specialty sample introduction techniques such as hydride generation and graphite furnace have greatly improved detection limits for a few elements.

## 2.2 Components of a Flame Atomic Absorption/Emission Spectrometer System

2.2.1 Overview: The general layout of optical components for a flame atomic absorption and emission spectrophotometer is shown in Figure 2-1. In FAAS, a source of pure light is needed to excite the analytes without causing excessive instrumental noise. Most instruments today use a hollow cathode lamp that is specific to each element being analyzed to emit a very narrow bandwidth of UV or visible radiation into the instrument for detection. All modern and some older atomic absorption systems use double-beam technology where the instrument splits the beam of source light, with respect to time, into two paths. One of these beams does not pass through the sample and is used to measure radiation intensity and fluctuations in the lamp, while the other beam is used to measure the radiation that interacts with the analyte. The splitting of the source beam is accomplished with a chopper, illustrated in Figure 2-2 where the chopper is in the reflection position in the center of the figure. The other half of the time, radiation is passed through the sample cell: in this case, the flame that contains the atomized gaseous metal analytes. A portion of the metal atoms absorbs a specific wavelength of radiation (matching the wavelength emitted by the hollow cathode lamp) that results in a quantitative reduction in the intensity of radiation leaving the sample cell. After interaction with the sample, or in the case of the reference beam bypassing the sample in the burner head, the beam of light is reflected by mirrors into the monochromator. This reflected light that contains various wavelengths past through a small slit that is size adjustable. Then it reflects off a focusing mirror to travel to the dispersing device (today a grating monochromator is used). Finally, the separated wavelengths of light are focused towards the exit slit with another focusing mirror. By changing the angle of the monochromator, different wavelengths of light enter the detector through the exit slit of the monochromator. The detector in most AAS units is a photoelectron multiplier tube (PMT) that amplifies and converts the signal of photons to electrons that are measured as an electrical current.

An emission spectrometer can be identical to an absorption system except that no external light source is used to excite the atoms. In flame emission spectroscopy, the electrons in the analyte atoms are excited by the thermal energy in the flame. Thus the sample is the source of photon emissions through relaxation via resonance fluorescence (Section 1.2.2). Note that this results in emission systems that are only single beam in design.

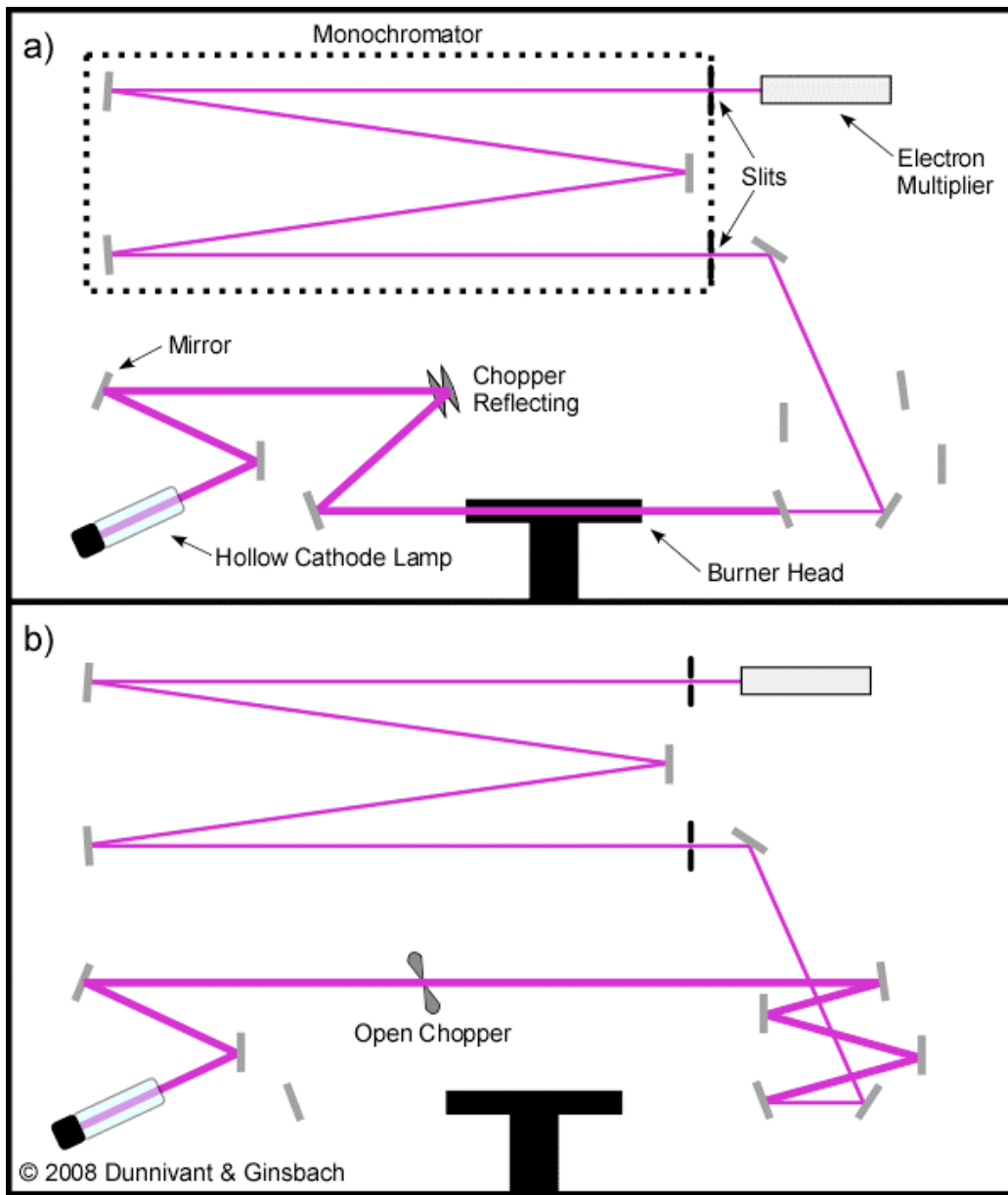


Figure 2-1. An Overview of a Flame Atomic Spectrophotometer. a) in detection mode where the source beam goes through the flame sample cell; b) in reference mode where the source beam bypasses the sample cell.

One modern and very important component not shown in Figure 2-1 is an automatic sampler. An automatic sampler is a device that is used to analyze numerous samples without the constant attention of an analyst. Modern automatic samplers can hold over a hundred samples. They can be used for most of the modes of FAAS and FAES. Instrument setup for running a set of samples with an automatic sampler is similar to the normal instrument setup: the correct lamp must be installed and aligned and the flame must be lit and optimized with respect to burner height. Software and instrument settings may also need to be adjusted to ensure a smooth run of samples. Of course, automatic samplers require the use of a computer to both run the automatic sampler and collect the relatively large amount of data produced from various samples. Automatic samplers greatly reduce the cost of analysis when large numbers of sample need to be analyzed for the same element. Usually an analyst will spend a normal day shift processing (digesting and diluting) samples. An instrument equipped with an automatic sampler can be set up at the end of the day and allowed to run all night without paying an analyst to manually run the samples or “baby sit” the instrument. In the morning, the analyst arrives with a collection of data to process.

2.2.2 Optical Radiation Sources: For FAAS and FAES, the wavelengths of interest are in the UV and visible range. There are three basic types of radiation sources that are utilized in these instruments: continuous sources, line sources, and laser sources. A continuous source, also referred to as a broadband source, emits radiation containing a broad range of wavelengths. A plot of intensity on the y axis and wavelength on the x axis is shaped like a broad Gaussian distribution with a few small peaks and shallow valleys. The emission wavelengths of a continuous source can range over hundreds of nanometers.

Examples of lamps considered to be continuous sources are deuterium, mercury, xenon, and tungsten lamps. These various lamps are used as background correction lamps (signal to noise correction devices) in AAS and AES instruments and not as source lamps for analyte detection.

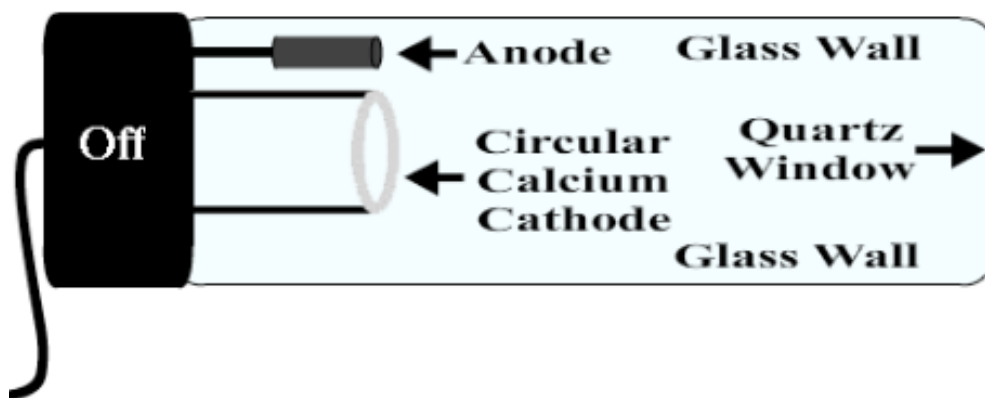
Line sources are lamps that emit very narrow bands of radiation, but this source of radiation is not as pure as radiation from a laser. The most common line source radiation generator used in AAS is the hollow cathode lamp (HCL). A schematic of a calcium HCL is shown in Animation 2.1 below. These lamps are encased in a cylinder made out of glass walls and a quartz end cap. Glass end caps can be used for visible wavelength emitting materials while quartz must be used for UV emitting HCLs. These cylinders are filled with a noble gas (Ne or Ar) to sub-atmospheric pressures of 1 to 5 torr. HCLs also contain a tungsten anode, a cathode composed of the metal of interest, and various insulators (usually made out of mica). Lamps containing more than one element in their cathode are also available but most FAAS and FAES instruments can only measure one element at a time.

A HCL works by placing a 300 V potential across the electrodes that generates a current of 5 to 15 milliamps (mA). As the electrons migrate toward the cathode, they collide with the noble gas atoms and ionize them. These charged noble gas atoms collide with the cathode. If the kinetic energy of the noble gas cations is high enough, some of the metal atoms on the cathode will be dislodged, producing an atomic cloud of metal in the gaseous phase. This process is referred to as sputtering. A portion of the collision energy will cause the gaseous phase metal atoms to enter into an excited electronic state. These excited gaseous-phase atoms relax from the excited state to the ground state through resonance fluorescence that emits a specific wavelength of UV or visible radiation (Section 1.2.2). This emission usually corresponds to only one or a few energy gaps that results in the generation of a relatively pure source of light. Higher currents can be used to generate more photons but too much current

results in self absorption of the photons and Doppler broadening of the bandwidth (a degradation of the spectral purity of the signal (Section 2.2.6)). A proper balance of current and generated radiation intensity allows for maximum sensitivity for absorption spectrometry.

While the use of a HCL is most common in AAS systems, other line source generators are available including lasers and electrode-less discharge lamps (EDLs) such as microwave EDLs and radiofrequency EDLs. Lasers produce the most pure form of radiation but are of little to no use in AAS or AES and thus, will not be discussed here because they are not tunable to the range of wavelengths needed in AAS. Lasers are utilized for sample introduction for inductively coupled plasma systems; this laser ablation technique is discussed in Chapter 4. EDLs are also relatively rare in AAS instruments and are only used for a few selected elements. In these lamps, the metal atoms are excited using microwave or radiofrequency generators. EDLs produce higher intensity radiation than an HCL but are generally not as reliable or commercially available for all elements of interests. As a result, most analytical technicians use HCLs in their FAAS systems.

Please view the animation of the hollow cathode lamp below.



## Animation 2.1 Animation of a Hollow Cathode Lamp.

### 2.2.3 Mirrors

Mirrors are important components of all spectrophotometers. Mirrors are used to direct radiation by reflecting it in a specific direction. Most atomic absorption units employ mirrors that reflect only UV and visible wavelength radiation. Mirrors are usually made of flat- or concave-shaped glass coated with a metal surface, usually aluminum. In some cases a plastic support can be used as the coating substrate. Metals are plated on the surface by a technique known as thin-layer vacuum coating. A variety of mirrors exist, including plane, concave, and collimating (a form of focusing). Recall from Section 1.3.1 that reflection is the interaction of radiation at the interface of two media with vastly different refractive indexes.

### 2.2.4 Chopper

A chopper is a device that splits a single beam of radiant light into two directions. A chopper is a circular-shaped device split into quarters (refer to the figure below). Opposing quarters of the chopper are open (contain no material as in the left-hand side of Figure 2-2) while the other quarters of the chopper contain a mirrored surface (as in the right-hand side of Figure 2-2) in order to direct the light to the sample cell (as shown in Figure 2-1). The chopper rapidly spins in the beam of light, directing the light by reflection as the mirror interacts with the light or by allowing the radiation to pass as the empty portion of the chopper moves past the beam of light. Thus, choppers split the beam of light with respect to time (as opposed to space where two adjacent mirrors would direct the light in two different directions). If the chopper spins faster than the fluctuation of noise in the source signal, an accurate measurement of the background noise can be obtained and corrected for in the sample readings.

The positions of the chopper and the resulting beam of radiation are illustrated in Figure 2-2.

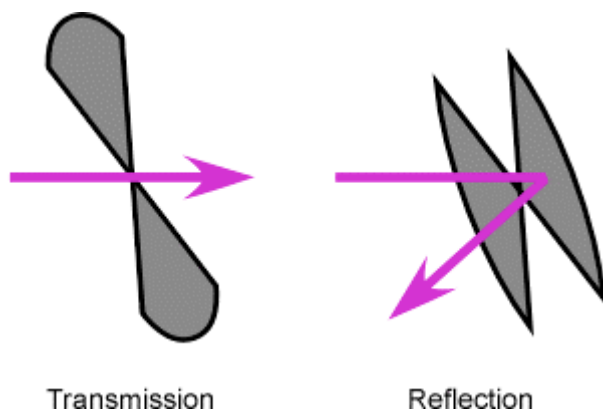


Figure 2-2 A Chopper, a Device used to Split Source Light with Respect to Time.

### 2.2.5 Burner Head

The burner head in FAAS and FAES systems is where all of the chemical reactions take place. The burner head, as shown in Animation 2.2, consists of an inlet tube; fuel and air inlets; a nebulizer; mixing cell; and the flame (the reaction and sample cell). Aqueous samples move through the inlet tube into the nebulizer which atomizes the liquid into small droplets. The mixture of sample droplets, oxidant, and fuel is homogenized by the mixing fins in the mixing cell before this mixture is atomized in the flame. The sample liquid is drawn into the nebulizer by a phenomenon known as the Bernoulli effect where a compressible fluid (the fuel and oxidant gases) is passed through a constriction in a pipe.

The Bernoulli principle is the pressure differential created when gases flow through a constriction. The gaseous flow, where the velocity is below the speed of sound, creates streamlines along the path of flow (represented by the horizontal lines in Figure 2-3). A streamline is an imaginary line that describes the path of a gaseous molecule through a system operating under laminar flow (a flow system with little random motion or mixing). The Bernoulli principle states that the sum of the mechanical energies along a streamline is the same at all

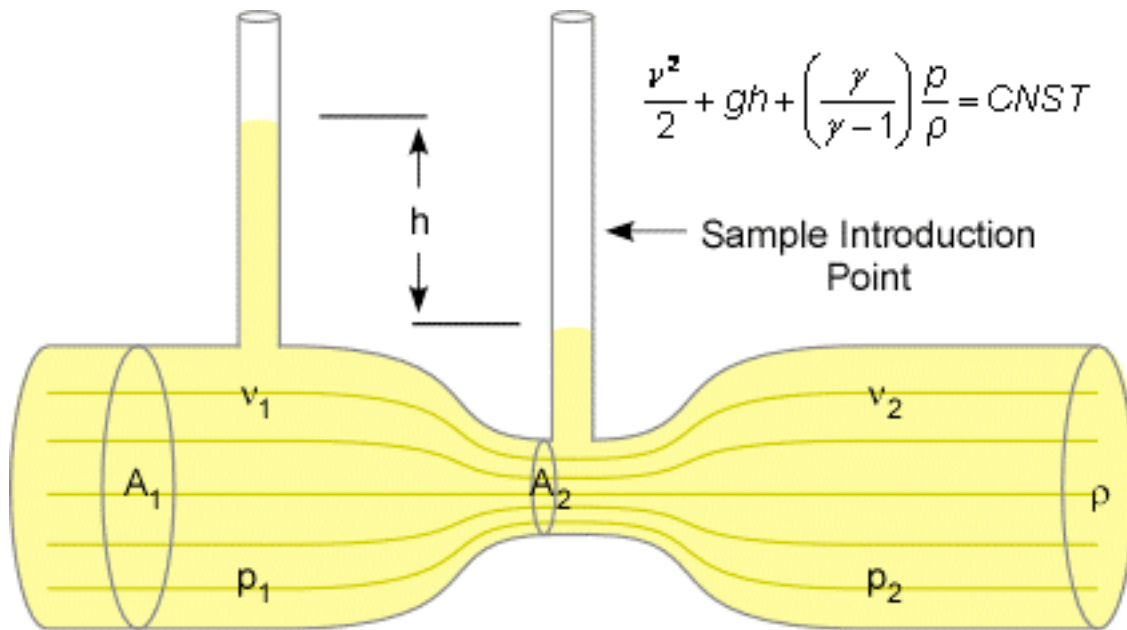


points on that streamline. This requires that the sum of kinetic energy and potential energy remain constant along the streamline. If the gas is flowing out of one reservoir (the reservoir with a larger radius) into a constricted reservoir, the sum of all forms of energy along the way is the same on all streamlines. The total energy at any point can be described by the following equation

$$\text{Total Energy} = \frac{v^2}{2} + gh + \left( \frac{\gamma}{\gamma - 1} \right) \frac{p}{\rho}$$

where  $\gamma$  is the ratio of the specific heats of the fluid,  $p$  is the pressure at a point,  $\rho$  is the density at the point,  $v$  is the speed of the fluid at the point,  $g$  is the acceleration due to gravity, and  $h$  is the height of the point above a reference plane. Since the total energy of the system must be conserved, the total energy must equal a constant for the system.

Consider a gas molecule moving from left to right along one of the horizontal streamlines in Figure 2-3. While all of the variables in the total energy equation change, it is necessary to only focus on the pressure and the velocity at a particular point. This is valid because the pressure and the velocity at a single point are the dominant contributors to the overall total energy. When this molecule moves from left to right it encounters less pressure and subsequently  $h$  becomes smaller. In order for energy to be conserved, the velocity ( $v$ ) must become larger. The converse is true when the particle moves farther right into an area of higher pressure. In this instance, the velocity must become smaller so the total energy of the molecule never changed over the entire system. As a result of Bernoulli's equation, the highest speed occurs at the lowest pressure, and the lowest speed occurs at the highest pressure.



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Figure 2-3 Diagram Explaining the Bernoulli Principle (A is cross sectional area, v is the fluid velocity, p is pressure,  $\rho$  is fluid density, and h is head pressure (or difference in pressure)).

The Bernoulli discussion (and Figure 2-3) is only illustrative of the general concept of pressure and flow balances. The design of the inlet chamber in AAS units is slightly different, but the principles of the Bernoulli equation cause the sample to enter into the mixing chamber in AAS and AES units. For the situations occurring in FAAS and FAES, if a fluid reservoir (the aqueous sample inlet tube) is connected to the low-pressure region of the fuel and oxidant gas inlet constriction, the lower pressure present in the constriction will draw fluid into the system (nebulizer chamber). A compression valve located on the sample inlet pipe is used to regulate the flow. As a result, the Bernoulli effect causes the liquid to freely move into the AAS without the use of a pump.

Next, the sample enters into the nebulizer, a mixing chamber where the sample is broken into an aerosol mist. The droplet size of this aerosol formed in the nebulizer is of importance since this directly affects how much analyte

reaches the flame. Droplets with diameters greater than 20  $\mu\text{m}$  are trapped in the spray chamber by attaching to surfaces and flow to the waste container. Only about 10% of the water that enters the nebulizer reaches the flame. The empirically determined governing equation for the determination of droplet size is

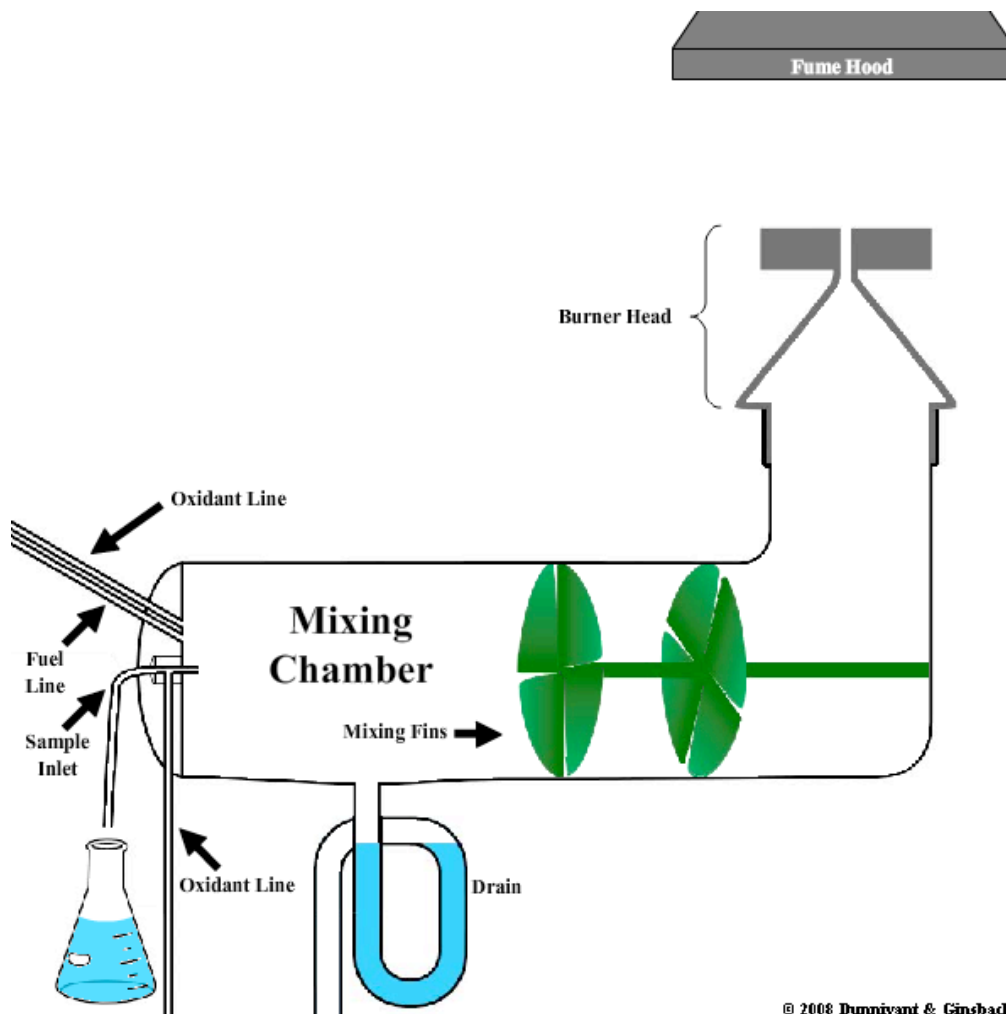
$$d_o = \frac{585}{v} \sqrt{\frac{\gamma}{\rho}} + 597 \left[ \frac{\eta}{\sqrt{\gamma\rho}} \right]^{0.45} 1000 \left( \frac{Q_{\text{liquid}}}{Q_{\text{gas}}} \right)^{1.5}$$

where  $d_o$  is the droplet size which is a function of viscosity ( $\eta$ ), density ( $\rho$ ), and surface tension ( $\gamma$ ) of the sample solution, the flow rate of the nebulizer gas ( $Q_{\text{gas}}$ ) and the aspirated solution ( $Q_{\text{liq}}$ ), and the velocity of the nebulizing gas ( $v$ ).

After the sample is pulled into the nebulizer and turned into an aerosol mist, it is mixed with the fuel and oxidant by two mixing fins. Common fuels used in FAAS and FAES units are acetylene (for hotter flames) and hydrogen (for cooler flames). Oxygen in the air or nitrous oxide is used as the oxidant to regulate the temperature of the flame. Different elements require different flame conditions, including the choice of fuel and oxidant and the ratio of the fuel to oxidant mixtures. Hydrogen-air flames produce temperatures of about 2000 °C, while acetylene-air flames yield temperatures of approximately 2300 °C and acetylene-nitrous oxide yield temperatures of 2900 °C. Within these fuel types, fuel-rich mixtures yield cooler flames and oxidant-rich mixtures yield hotter temperatures. Temperatures are optimized for a particular analyte since different metal elements are excited or atomized under different conditions. In addition, some metals readily form oxides in an oxygen rich atmosphere, a reducing (fuel rich) environment is necessary to produce atomic instead of molecular species (such as oxides). Other elements are stable in the atomic state under any fuel/oxidant mixture. After this specific mixture of fuel and oxidant are mixed together with the sample, they exit the burner head and pass into the flame.

Several processes and reactions occur rapidly when the sample molecules enter into the flame. First, the water is evaporated and removed from the metal complex. Next, the heat of the flame degrades organic and dehydrated inorganic complexes into gaseous atomic states (ground electronic states) that are then excited by the thermal energy in the flame. In the lower portion of the flame, absorption of photons occurs by the electronic ground state gaseous atoms. As the analytes rise into cooler regions of the flame, the excited atoms relax and emit a photon for emission spectrometry. Finally the fumes and metals from the flame are removed from the laboratory by a fume hood exhaust system.

Please review the animation of the sample introduction system and the burner head in Animation 2.2.



Animation 2.2 Illustration of an Aqueous Sample Introduction into a Burner Head.

### 2.2.6 Instrumental Noise in the Source Lamp and Flame

Now that the source lamps and flames have been introduced, it is time to discuss sources of noise in AAS measurements; some of these also apply to AES measurements. FAAS and FAES instruments usually start with a pure source of light, and it is desirable to end with that same wavelength in as pure of a form as possible. Noise results when this process breaks down and the intensity of the wavelength of interest decreases or impure radiation reaches the detector. Decreases in the quality of light occur as the radiation passes through air and at the interfaces of surfaces (Section 1.3). In addition, there are three common causes of line broadening: natural, Doppler, and pressure broadening.

*Natural broadening and the Uncertainty Effect:* Natural broadening of pure spectral lines occurs due to the finite amount of time an atom spends in its excited electronic state. As the absolute time of the two states (ground and excited) approaches infinity, the width of the line resulting from a transition approaches zero; this is a direct result of the Heisenberg Uncertainty Principle for time and energy.

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

For example, the time required for absorption of a photon by an atomic species is approximately  $10^{-15}$  seconds, while the lifetime of the excited state is about  $10^{-9}$  seconds. This excited state transition is sufficiently short enough that the uncertainty in energy is greater than  $10^{-25}$  J. For UV and visible wavelengths in the system discussed here, the line broadening from this uncertainty in energy affects the wavelength by  $10^{-5}$  to  $10^{-6}$  nm, and is considered negligible compared to other forms of line broadening.

*Doppler broadening:* The Doppler shift of a wavelength is an important observation in physics. This broadening is caused when an object is moving with respect to a detector while it simultaneously is emitting a wave such as a photon or sound. The observed wavelength will be slightly different when the emitter is moving towards or away from the detector. Everyone who has listened to a train whistle at a railroad crossing has observed this principle; as the train approaches a stationary observer the sound frequencies are compressed and a slightly higher frequency is heard. In contrast, as the train passes the observer the frequency is broadened and a lower frequency pitch results. For the instruments discussed in this text, the Doppler effect is observed only in a hollow cathode lamp. If an excited atom is moving toward the sample cell and detector, a slightly shorter wavelength will be observed while an atom moving away from the detector will emit a longer wavelength. This is also referred to as thermal motion. Even though atomic speeds are significantly less than the speed of light (1000 m/s), this effect can result in spectral broadening since the wavelength of interest may now overlay with another wavelength present in the sample or flame. The net result is an increase in noise and possibly an overlap with another absorbing or emitting atomic species. For the conditions in common FAAS flames, the width of a spectral line is about two orders of magnitude greater than the breadth present in the natural occurring line due to natural broadening. This is calculated for individual wavelengths by

$$\Delta\nu_D = \nu/c (2RT/M)^{0.5}$$

where  $\nu$  is the frequency of interest,  $R$  is the ideal gas law constant,  $T$  is temperature and  $M$  is the atomic mass of the element. For typical operating conditions, the broadening caused by the Doppler Effect is about  $10^{-4}$  nm. This effect accounts for most of the line width broadening in flame-based instruments.

*Pressure broadening:* Pressure broadening, also known as collisional or Lorentzian broadening, results from collisions between the gaseous atom of interest and any other atom. Collisions result in radiation-less relaxations by distributing electronic energy into vibrational and rotational energy that lengthens the wavelength of the line as compared to its central frequency (unaffected frequency or wavelength in a vacuum). Pressure broadening can occur in the lamp and the flame in an AAS instrument. In a source lamp, such as a hollow cathode lamp, most collisions are between gaseous sputtered metal atoms and the noble gas. The pressure of Ar or Ne in the source lamp is very low to decrease the frequency of these collisions; most of these collisions result from other gaseous sputtered metal atoms present in the source lamp. The net result is a line broadening of approximately  $10^{-6}$  nm and is much less significant than the Doppler Effect (approximately  $10^{-4}$  nm). The observed two order of magnitude difference illustrates the lack of importance of pressure broadening in hollow cathode lamps. However, in high-pressure background source lamps, such as deuterium, Hg and Xe lamps, collisions are more common and the resulting broadening is capitalized upon to emit a broad range of wavelengths in the UV and visible regions. In the flame, the reaction cell used in most AAS units, collisions occur between the analyte of interest, fuel and oxidant molecules and other ions.

2.2.7 Slits: After the radiant light has passed through the sample it is directed by mirrors to the entrance slit of the monochromator. A slit is nothing more than a hole or slot in a black surface that allows a narrow beam of light to pass through it. The purpose of an entrance slit is to only allow a fine beam of light to enter the monochromator. After the monochromator separates the white light into its components, and a narrow band of wavelengths is directed through the exit slit. This allows only a narrow band of wavelengths to exit the system and reach the detector.

## 2.2.8 Monochromators

As discussed in Chapter 1, a monochromator is a device that is used to separate wavelengths of light through dispersion. There are two types of monochromators: prisms and grating systems. Despite achieving the same goals, as noted in Chapter 1 prisms and grating systems separate various wavelengths of light in different fashions. Prisms refract light at the interface of two surfaces with differing refractive indexes creating angular dispersion. Historically, prisms were the first monochromators to be developed, but they have limitations. Their resolution is significantly lower than a grating system and their separation technique is non-linear (with respect to distance along the exit slit) which creates mechanical problems with focusing a specific wavelength on the exit slit. The one advantage that prisms possess over grating systems is their low manufacturing cost.

Diffraction gratings are materials with a large number of parallel and closely spaced slits or ridges. Diffraction causes constructive interference at unique points for each wavelength. In Section 1.3.5 the theory behind the two governing equations for diffraction yielding constructive interference was described by

$$n \lambda = d(\sin i \pm \sin r)$$

with each of the variables shown again in Figure 2-4. Despite their higher cost grating monochromators are used in all modern medium- to high-end spectrometry systems.



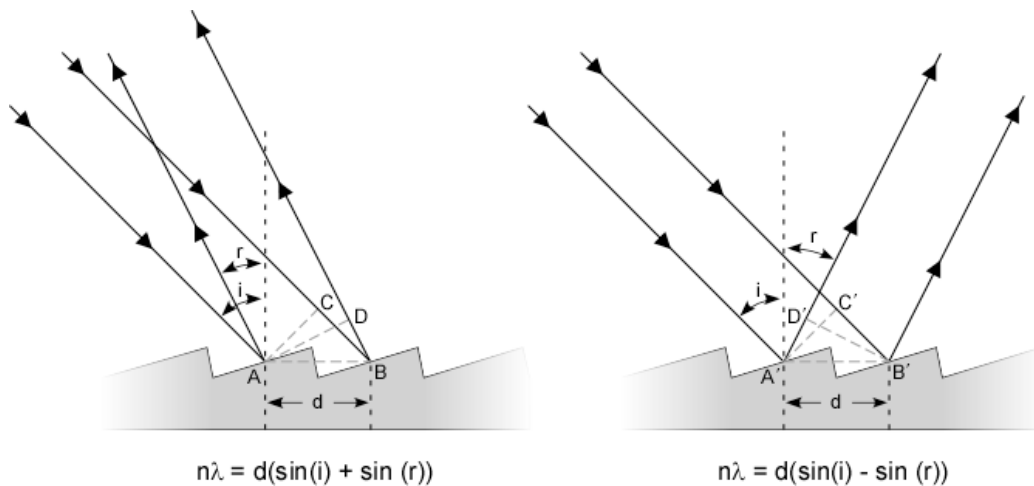


Figure 2-4 Diffraction Resulting from a Typical Echellette-Type Grating.

This equation was simplified for an Echelle style grating to

$$n \lambda = 2d \sin \beta$$

The first grating monochromators used were of the Czerny-Turner style illustrated in Figure 2-5. This common form of monochromator was used for decades when PMTs (Section 2.2.9) were the detector of choice. UV and visible wavelengths enter the monochromator through an entrance slit where they are reflected onto the grating device where spectral separation occurs. The separated wavelengths were collimated (focused by wavelength) with a concave mirror toward the exit slit. The tilt angle of the grating device determined the band of wavelengths exiting the monochromator and reaching the detector: usually a photomultiplier tube (PMT).

Today, with the replacement of PMTs in higher-end instruments by more modern microelectronic circuitry (charge transfer and injection devices described below), only an entrance slit is necessary. In some higher-end AAS and AES units, newer monochromator/detector systems have an Echelle grating monochromator and charge transfer device placed together where all wavelengths are measured simultaneously with a charge transfer device without

the need for an exit slit (illustrated in the next section). This can also be used in absorption spectrometry where individual source lamps are required (only one element is still detected at one time), but is mostly of importance in emission spectrometry where all elements present in the sample cell are undergoing wavelength specific relaxations.

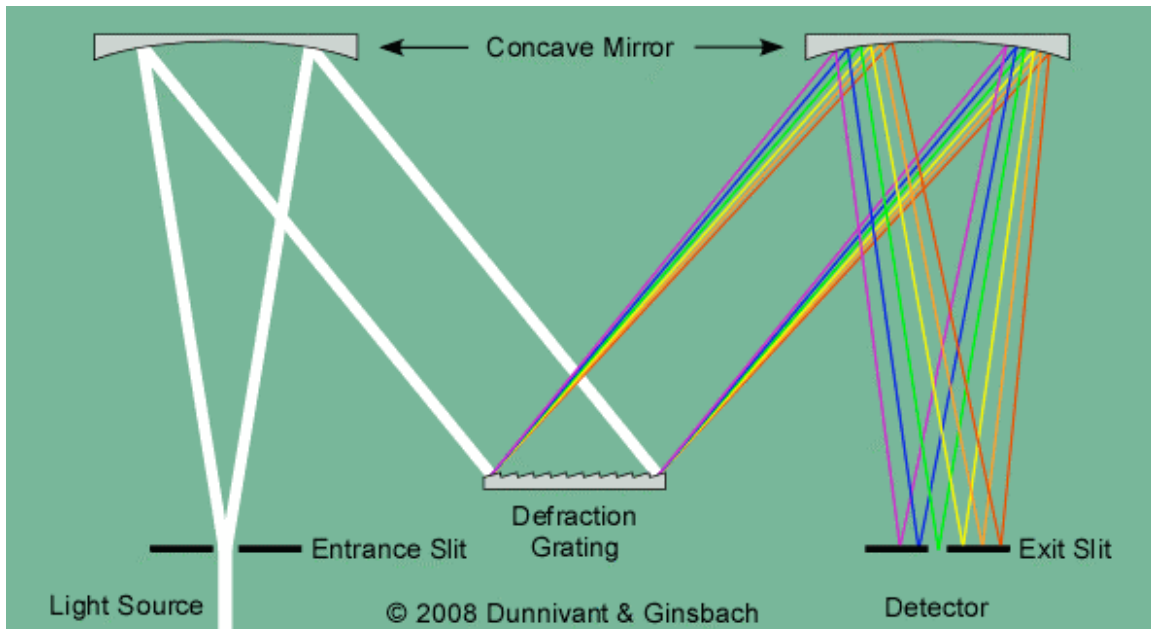
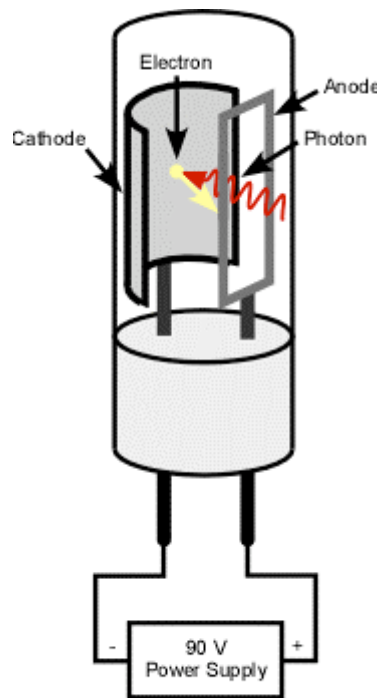


Figure 2-5 A Czerny-Turner Style Grating Monochromator. Note that only two diffracted beams of light are shown leaving the diffraction grating but identical beams leave each blazed surface and are collimated by a concave mirror onto the exit slit as one rainbow of wavelengths.

## 2.2.9 Detectors

AAS and AES measurements require that the energy contained in a photon to be converted into a measurable electrical signal. Early detectors relied on a more solid-state version of the photoelectric effect that is best illustrated by a phototube, one of the first detectors to convert radiant energy to electrical energy.

Phototubes: Figure 2-6 shows a diagram of a basic phototube (PT). A PT consists of an evacuated glass or quartz chamber containing an anode and a cathode. Cathode surfaces are composed of materials that readily give up electrons; Group I metals such as Cs work well of this purpose. A relatively large potential is placed across the anode and cathode, usually 90V, and the gap is referred to as a dynode. Electrons contained in the cathode are released as photons with a sufficient energy strike the surface. This causes electrons to move through the low-pressure gap to the anode, which produces a current. For a PT, a single photon causes only a single electron to be measured. For emission spectroscopy, the magnitude of current produced by the cascade of electrons in the detector is directly proportional to the concentration of analyte in the sample.



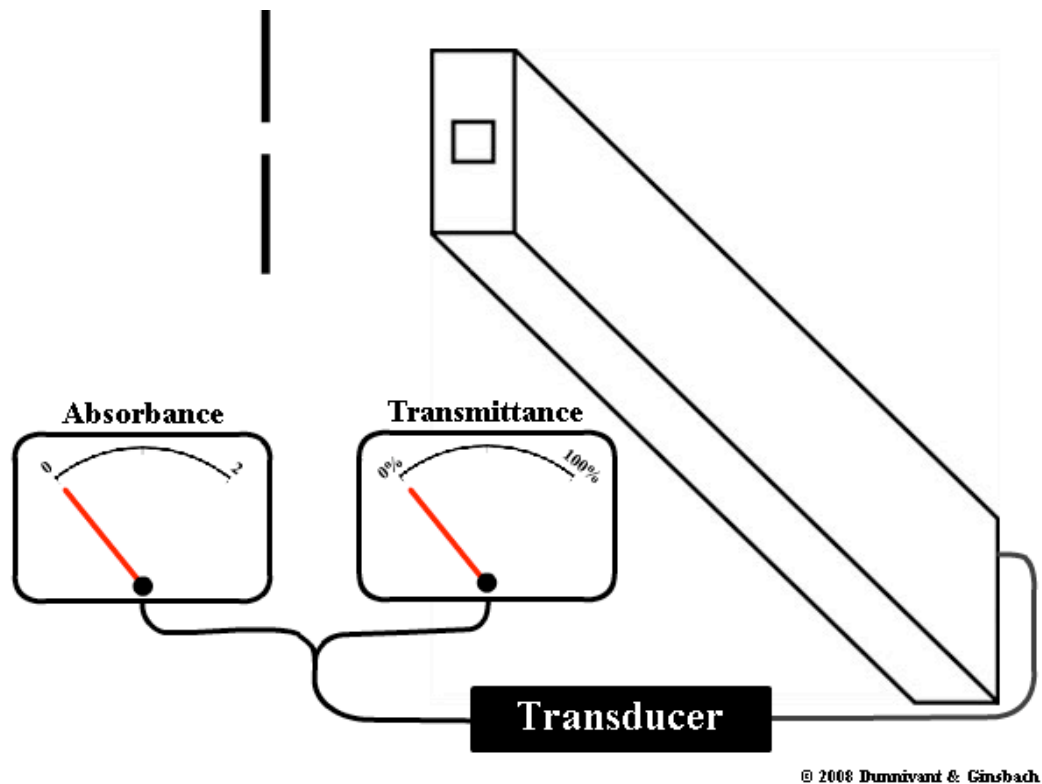
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Figure 2-6 Diagram of a Phototube.

Photomultiplier Tubes: Photomultiplier tubes (PMT) are an extension of the phototube where numerous dynodes are aligned in a circular or in a linear

manner. Here most of the electrodes act as both an anode and a cathode with each dynode (electrode pair) having a potential difference of +90 V; thus, the potential increases by 90 V as an electron goes from one electrode to the next (refer to Animation 2.4 below). When nine dynodes are used, a common feature in PMTs, the net result is a yield of  $10^6$  to  $10^7$  electrons from a single emitted photon. This causes considerable amplification of a weak signal compared to a photon tube that does not amplify the signal. PMTs were excellent detectors for FAAS and FAES measurements due to the low intensity of radiation in these systems and have dominated these instruments for decades.

In Animation 2.3 below, only discrete packets photons are shown entering the detector from a chopped signal; this is only for illustration purposes since the stream of photons and the generated electrons are continuous producing an analog signal. Photons enter through a slit, strike the first cathode that is positively charged and a small number of electrons are produced. These electrons jump the gap to the next electrode where each arriving electron produces even more electrons due to the increased potential placed on the surface. This process is repeated over and over until a current is read at the anode (the final electrode). Play Animation 2.3 at this time.

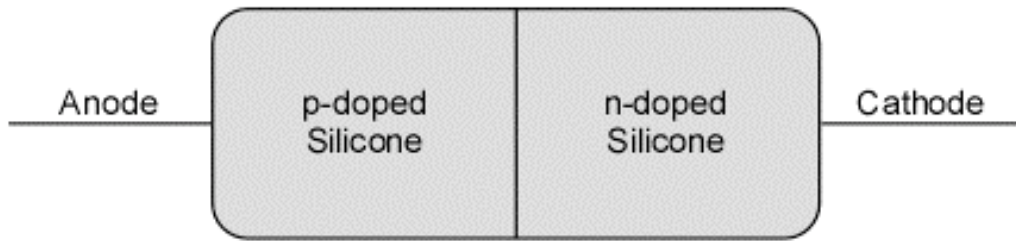


Animation 2.3 Illustration of a Discrete Electron Multiplier.

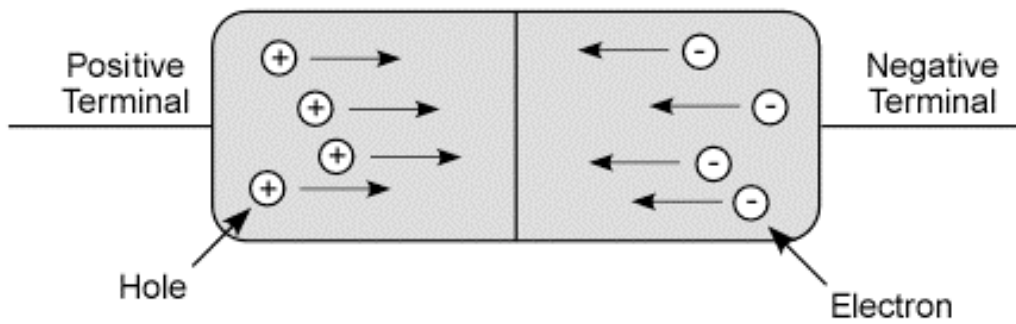
Charge Coupled Devices: In the mid-1990s, a new style of photon detector (and collector) was developed and implemented into instruments because of advancements in computer chip technology that decreased cost of producing these chips. Before charge coupled devices (CCDs) can be understood and appreciated, the historical development of photosensitive computer chips must be presented.

The development of advanced detectors starts with a silicon diode device. A diode is an electronic device composed of two electrodes that can either act as a resistor or a conductor depending on the potential placed on the device. Such a device is shown in Figure 2.7a.

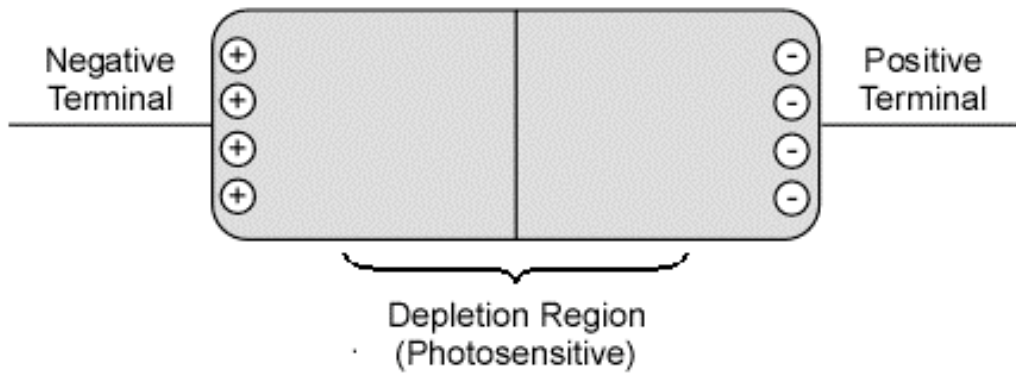
a)



b)



c)



d)

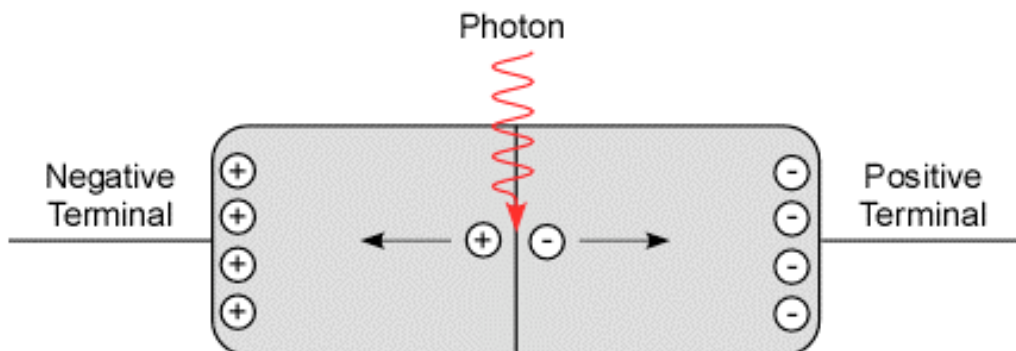


Figure 2.7 A Basic Silicon Diode. (a) with no applied voltage. (b) with a forward (positive) bias placed on the electrodes. (c) with a reverse (negative) bias placed on the electrodes. (d) the current generation resulting after a photon strikes the depletion region.

A silicon diode consists of two pieces of silicon, one positively doped (p-doped) and one negatively doped (n-doped), with the functional area (the depletion region) being at the interface between the two media. The positively doped end was created by doping (replacing) an occasional Si atom with a Group III element, such as aluminum. The net result is referred to as a positive charged carrier that can move through the chip, or an electron hole since one bond is missing between Al and Si. In contrast, the negatively doped end of a diode is a similar piece of silicon where occasional Si atoms have been replaced with a Group V element, such as phosphorus. The net result is the creation of a negatively charged carrier since this material contains extra electrons.

Combining the p-doped and n-doped silica into one device (called a pn junction) creates a diode that can be operated in two modes, forward and reverse bias. In the forward bias mode, a positive potential is placed on the p-doped semiconductor and a negative potential is placed on the n-doped semiconductor (refer to Figure 2.7b). This results in the holes and electrons moving toward the center of the device where they can combine and reduce the resistance in the diode; here the device acts as a conductor. The forward bias mode is of no interest in detectors utilized for spectrometry.

Figure 2.7c shows the silicon diode when a reverse bias is placed on the device. Here, the charges on the electrodes are reversed and the holes in the p-doped semiconductor are drawn toward the negative terminal while the electrons in the n-doped side are drawn toward the positive terminal. This results in the creation of a depletion area at the interface of the two semiconductors, where there are few holes or electrons in the matrix. As a result of the voltage barrier,

high resistance is created which allows minimal electric current to cross the p-n junction; in this mode the device acts as a resistor. In this mode of operation, when a photon of sufficient energy (in the UV, visible, and near IR regions; photons with wavelengths from 190 nm to 1100 nm) strikes the depletion region, holes and electrons are created that then migrate to their respective terminals generating a current (Figure 2.7d). The amount of current generated is directly proportional to the number of reactive photons striking the depletion region. Thus, these devices can be used in the detection and quantification of radiant intensity. Silicon diodes are more sensitive than the older vacuum-style phototubes but their performance is still poor when compared to PMTs described earlier (due to the lack of amplification). The advantage of a silicon diode is the large numbers that can be placed in a linear arrangement referred to as a linear diode array (LDA).

**Linear Diode Arrays:** A linear diode array allows the simultaneous detection of a wide number of wavelengths. When a linear diode array is utilized, UV or visible light is first separated by a monochromator and the separated wavelengths are aligned onto the surface of a linear diode array with a collimating mirror or lens. Figure 2-8 illustrates a section of a linear arrangement of up to 400 individual diodes. Each wavelength of interest is positioned on one of these many p-n junctions allowing the intensity of each wavelength to be measured simultaneously. The entire UV and visible spectrum can be measured with considerable wavelength resolution with one LDA.



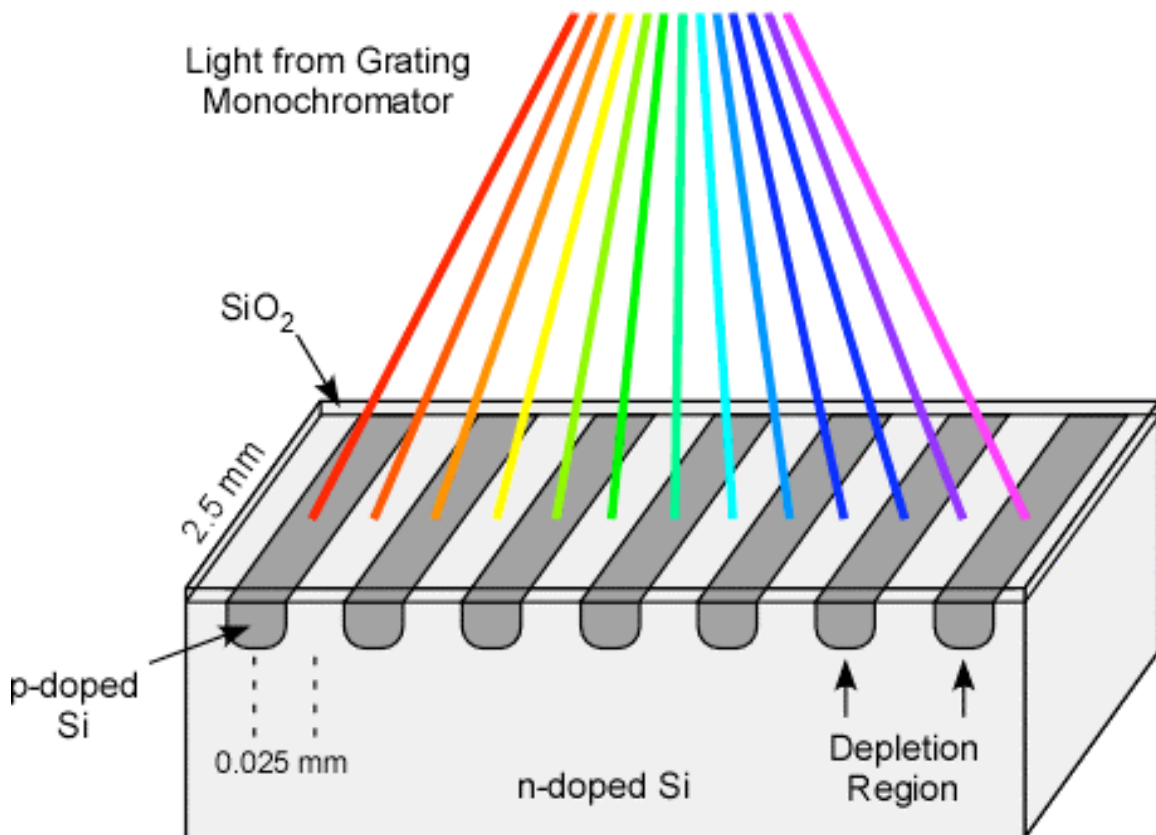


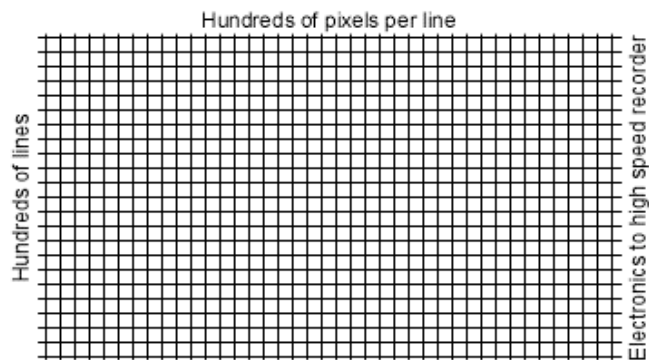
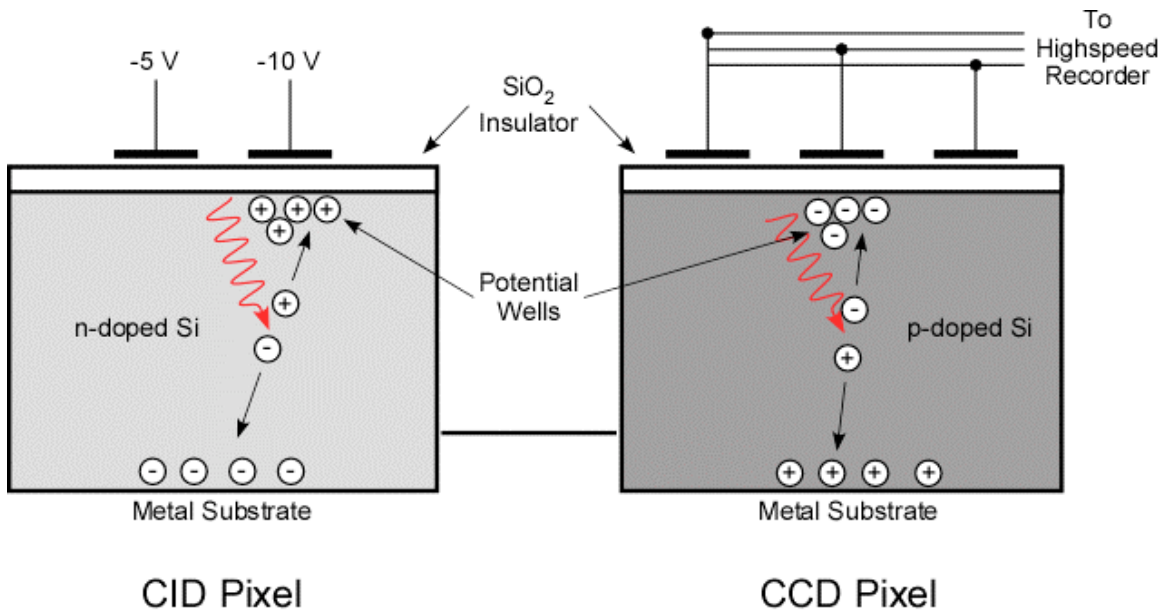
Figure 2-8 A Linear Diode Array. Each p-n junction, the interface between shaded regions, is a diode.

LDAs offer the advantage of measuring all wavelengths in a sample at the same time, which is especially important in emission spectrometry. This type of detector is commonly used today in instruments where detection limits are not a problem since LDAs do not amplify the original signal. Common uses include UV-visible detectors in inexpensive spectrometers and in many high performance liquid chromatography (HPLC) systems. The cost of production has greatly decreased in recent years and the cost of an LDA is now cheaper than a PMT, however PMTs have higher sensitivity, a larger dynamic range, and lower signal to noise ratios. In selecting between a LDA and a PMT detector one must weigh the benefit of simultaneous wavelength detection versus detection limit. LDA are most commonly used in absorption spectroscopy, but are not currently offered in common, more inexpensive FAAS or FAES systems. Diodes and linear diode

arrays are mentioned here to aid in the understanding of charge-transfer devices, which are commonly used in AAS and AES today.

Charge-Transfer Devices: There are presently two types of charge transfer devices (CTDs), charge injection devices (CIDs) and charge coupled devices (CCDs). Both of these overcome the disadvantages of LDAs (low dynamic range, poor sensitivity, and low signal to noise ratios) by amplification (through timed storage or accumulation) of the original signal. As a result they can match the performance of PMTs and actually exceed them by simultaneous detecting multiple wavelength including separating different orders of diffraction. As a result of these advantages and due to the recent reductions in production costs and spatial constraints, CTDs are rapidly replacing PMTs.

CTDs are one- or two-dimensional arrays of detectors that can offer thousands of individual detector pixels. Both p-doped and n-doped semiconductors are used and individual pixels for each are shown in Figure 2-9.



### CCD Array

Figure 2-9 p-doped and n-doped pixel Charge Transfer Devices. (a) a Pixel for a Charge Injection Device (CID). (b) a pixel for a Charge Coupled Device (CCD). (c) an Array of CCDs (each pixel is a detector).

Charge injection devices (CIDs) use n-doped silicon (refer to Figure 2-9a). When a photon of sufficient energy strikes a bond in the silicon, a hole and an electron are created. The electron migrates to the positively charged substrate and is removed from the system. The hole migrates to a “potential well” that is created under the most negatively charged electrode. The system, as shown in Figure 2-9a acts as a capacitor because of the -5V and -10V applied potential. It

is important to note that each “well” can accumulate between  $10^5$  to  $10^6$  charges per electron; this closely matches the performance (amplification) of PMTs discussed earlier. Note that the silicon and electrode are separated by a non-conductive silicon dioxide layer. After a sufficient amount of time (when a large number of holes have been created and collected) the applied electrical potential on the -5V electrode is removed and a voltmeter (potentiometer) is used to measure the capacitor potential under the -10V electrode. The capacitor potential is directly related to the number of holes collected. If sufficient counts are measured the holes are cleared from the CID and a new measurement is started. The advantage of CIDs is that counting can be continued by reestablishing the -5V connection. Thus, amplification of the signal, or more specifically accumulation of holes, can be completed in two ways, (1) by initially measuring a significant amount of time and (2) by measuring and deciding to continue the collection process. This process is non-destructive, thus, the accumulated signal can be read repeatedly until a desired magnitude is obtained. When placed in a 2-dimensional array, they can contain tens of thousands of pixels and each pixel can be positioned to collect data for a specific wavelength from the monochromator. Due to high thermal noise CIDs are usually cooled to liquid nitrogen temperatures.

Charge coupled devices (CCDs), invented in 1969 at Bell labs, are designed in an opposite manner as compared to CIDs. In CCDs, p-doped silicon is used and the electrodes atop the semi-conductive material are positively charged. An individual pixel for a CCD is shown in Figure 2-9b. Here, photons strike the doped silicon, holes are neutralized and removed by the metal substrate below the pixel and electrons migrate to the potential well where they are stored. Arrays are read from left to right by shifting the potential on the electrons and measuring the potential charges transferred between the electrodes. Again the system (each pixel) acts as a capacitor where its potential can be measured by removing the applied potential and measuring the capacitor potential with a voltmeter. An individual pixel consists of three electrodes (a

three-phase clock circuit) that are used to sweep the charges to the right where they are moved to the next pixel and on to a high-speed shift register and then on to a preamplifier and readout. This allows for a pixel-by-pixel and row-by-row two-dimensional detector surface to be created. However, the measurement is destructive, unlike in CID detectors, so only one measurement is possible. This is not a disadvantage in FAAS or FAES measurements since a manual measurement only takes seconds to obtain, and doubling or tripling the reading time is relatively insignificant. For automated sample introduction, the increased data collection time is trivial. For most purposes, typical accumulations of the signal by CCDs match the amplification performance of PMTs.

For purposes of reference in spectrometry instruments, a CCD array (illustrated in Figure 2-9c) is about 1 cm by 1 cm in size and can contain up to approximately 20 000 pixels. Contrast this to the surface area needed to obtain the same resolution; one would have to position 20 000 PMTs at the proper angle with respect to the monochromator with each PMT being about 1.5 cm in diameter and 8 cm in height. The small size of the CCD array allows it to be placed inside the monochromator after a collimating mirror or lens and an exit slit is not required. Instruments with CCDs are significantly smaller in size, thus, less bench space is needed in the laboratory.

The two-dimensional nature of CCDs will be of more importance in the next chapter where inductively coupled plasma—atomic emission spectrometry (ICP-AES) is discussed. In ICP-AES, two dimensional reading devices are necessary to reduce interferences by allowing second and third diffraction orders that overlap in one dimension to be separated vertically onto the two dimensional array of a CCD.

As an interesting side note, CCDs are the imaging detector in older digital cameras, fax machines, advanced telescopes and many other imaging instruments. Here, like in spectrometry, an analog (continuous) signal is

segmented into a digital or pixilated image. Arrays used in high-end (expensive) cameras can offer the same resolution as extremely low ASA rated emulsion camera films. The array can contain millions of pixels and a color grid on the array allows for color photography. As soon as an analytical instrument is placed into production, development of the next model is underway. For example, CCDs, a remarkable detector in advanced FAES instruments will soon be replaced by complementary metal oxide semiconductors (CMOS) detectors. The limitations of CCDs are the time requirements for amplification and the relatively slow and spatial dependent readout of the signal. CMOS detectors have readout circuitry built into each pixel and each pixel can be randomly addressed and read. This enables relatively fast readout speeds. Lower end CMOS detectors are already in modern cell-phone cameras. More advanced CMOS detectors will have low noise, high speed data collection and readout, and a broader dynamic range.

#### 2.2.10 Instrumental Noise in Detectors

Chemists have little difficulty when they are measuring high concentrations of an analyte, but this situation is relatively rare. Most analysts attempt to determine if an analyte is present or not, and in doing so must measure the smallest amount of an analyte in a sample near the detection limit of the instrument. In many areas of science, such as environmental, forensics, and biological applications, the analyst is always struggling to lower the detection limit. This is referred to as “chasing the detection limit” since one of the goals of instrumental manufacture is to improve instruments to measure smaller and smaller quantities of analytes. The detection limit is basically the minimum concentration that one can measure above the “noise” in an instrument. To fully understand this concept, different types of noise must be discussed.

Environmental noise consists of factors in the immediate lab environment that will affect an instrument or sample. Obviously if an instrument is sensitive to

vibrations, such as an NMR, one would not place this instrument in an area of high vibration, such as next to an elevator. Similarly an analyst would not want to make delicate ppm-, ppb-, and ppt-level concentration measurements in an environment where the analyte of interest is present in high concentrations (such as in the air near a metal smelter). Most environmental noise with respect to metal contamination can be avoided by locating the sample preparation area away from the instruments or locating each in a clean room or HEPA hood.

Chemical noise tends to be unavoidable and specific to each analyte. One of the simplest types of chemical noise, that is completely unavoidable, is the electronic and vibrational fluctuations present in an atom or compound due to the Maxwell distribution of energies. These result in broad UV-visible absorption and emission spectra in aqueous samples but are of little consequence in gas phase transitions experienced in AA and ICP. Other forms of chemical noise include slight temperature and pressure fluctuations that affect measurements.

Instrumental noise is common and in many cases can be avoidable or managed. Instrumental noise is separated into three categories: thermal, shot, and flicker noise. Thermal noise (also referred to as Johnson noise) results from the thermal agitation of electrons in resistors, capacitors, and detectors. Most of the thermal noise can be overcome by cooling specific components of the instrument such as is done in advanced detectors (i.e. charge injection devices). Shot noise results from a current being generated by the premature movement of electrons across a junction. The best example is an electron being emitted from a photoemissive material, such as in photocells or electron multipliers that are used to measure the intensity of visible and UV light. There are a few electronic ways of minimizing shot noise, but these are beyond the scope of our discussion here. Flicker noise results from random fluctuations in current and is inversely related to frequency. Flicker noise is overcome by electronically modulating the detector output signal to a higher frequency where less noise is present (i.e. from  $10^2$  Hertz to  $10^4$  Hertz).

In practice, the analyst is concerned with distinguishing between a real signal and instrumental noise, quantified as the signal to noise ratio. Signal to noise is mathematically defined as

$$\frac{S}{N} = \frac{\text{mean of signal}}{\text{s.d. of signal}} = \frac{x}{\text{s.d.}}$$

where S is the mean of approximately 20 blank measurements and N is the standard deviation of these measurements. From a statistical standpoint, it should be noted that S/N is equal to the reciprocal of the relative standard deviation (RSD).

Two approaches are used to minimize noise: hardware and software. Common hardware approaches that are used to decrease noise are (1) grounding and shielding components and detectors, (2) using separate amplifiers for different signals, (3) placing frequency or wavelength filters “up line” from the detector, (4) modulating the instrument signal to a “clean” frequency, and (5) chopping the signal to obtain a reference reading of the background that can be subtracted from the sample signal. For spectroscopy, one of the most common software noise reduction techniques is to take as many readings as reasonably possible. The observed signal to noise ratio (S/N) is a function of the number of readings (n) taken as shown by

$$\frac{S}{N} = \sqrt{n} \frac{S_x}{N_x}$$

where  $S_x$  and  $N_x$  are the signal and noise readings for a specific setting. Note that as one takes more readings the S/N decreases by the square root of the number of measurements. By taking two measurements, one can increase the S/N by a factor of 1.4; or by taking four measurements the analyst can half the



noise. For the topics covered in this Etextbook, FAAS, ICP-AES, and ICP-MS instruments generally allow for multiple measurements over 5 to 10 seconds to be taken and averaged. And of course, the analyst can always analyze a sample multiple times given the common presence of automatic samplers in the modern laboratory.

### 2.2.11 Data Processing

Data collection has greatly advanced with the aid of computer technology that has replaced the strip charts of the decades before. But with this change other adjustments have been necessary. For example, almost all instrumentation signals are analog in nature (a continuous stream of data), while computers require data to be in a digital form (segmented). One of the best analogies used to explain the difference between analog and digital comes from the music recording industry. Vinyl records from the pre-1985 era were analog recordings, the music (grooves in the vinyl) was a continuous source of sound just as a guitar string continuously vibrates. Digital recording takes the analog input and breaks it into very short bits (segments), so short that most human ears cannot detect the individual segments (others argue, such as Neal Young, that compact discs (CDs) are the worst thing to happen to the recording industry due to a decrease in sound quality). This same analog to digital (A to D) conversion must take place before a computer can record and process data from an analytical instrument.

Computers have unquestionably allowed more control and extended capabilities of analytical instrumentation. Examples include the automated nature of the instrument, operation of automatic samplers, automatic collection and processing of data including automatically generating calibration lines and reporting concentrations of analytes in samples as opposed to detector response. However, in some ways computers have decreased operator knowledge of the instrument; two examples are the lack of knowledge concerning

the “nulling or zeroing” an instrument and “balancing” electronics of a system to optimum values. Prior to the addition of computers to instrumentation, these functions were manually adjusted, while today they are part of the automatic setup.

As an example, the operation of a typical FAAS blank and sample measurement will be used. Recall that in this system, a source lamp is split into two beams, one reference and one passing through the sample. Both beams go through the monochromator and to the detection where the reference and sample signal is processed separately. Finally an absorbance reading is displayed and recorded for each blank and sample. But notice, the blank and reference readings allow all of the source radiation to pass through the instrument unhindered (defined as 100 percent transmission), thus, generating a maximum response from the PMT detector, yet the reading displayed on the instrument panel is 0.000 absorbance units. Hence, there are unnoticed calculations and corrections going on “behind the scenes” in the instrument. What actually happens is the instrument sets the reference or blank sample to read a maximum signal (maximum number of electrons being generated by the PMT). Recall that the signal is rapidly chopped into reference and sample readings. Next, the instrument measures the signal for the sample, subtracts the reading of the blank from the sample, and the difference is the absorbed signal. Thus, readings go from low to high absorbance values.

It is also important to note that for systems such as FAAS units, electrical components that interact with each other must be “balanced” where signals, voltages, and currents must be optimized and matched between components. For example, when a hollow cathode lamp is turned on, the current placed on the electrodes is set to give out the maximum radiant output that the other instrument components can take but not damage the lamp by over heating or removing too much of the cathode material. The intensity of this radiant signal is adjusted further by increasing or decreasing the size of the entrance and exit slit on the

monochromator. Finally the “gain”, the electrical potential applied to the PMT dynodes, is adjusted as to provide maximum amplification but not overload the PMT. Today this is all adjusted automatically, but the process should still be understood.

Most computer-controlled systems operate the instrument using two computer programs: a method and a sequence. The method program controls physical conditions of the instrument such as lamp current, fuel and oxidant flows, and electronic gain placed on the PMT. Once the instrument is operating at its maximum performance, a sequence is started. A sequence is a program that tells the instrument what samples to run, where they are located in the automatic sampler, and what order to run the samples. The sequence also collects and stores the data for each sample in a separate file. Finally, the method is used again to calibrate the instrument using the data from the reference standards and to calculate the concentration of analytes in the samples (convert detector response to concentration).

Overall, computers are a significant asset to analytical instrumentation. They have increased the capabilities of instruments and significantly decreased the cost of analysis through the operation of automatic samplers and through advanced data processing. An additional aspect of data processing is the elimination of the need to re-type data into a spreadsheet or report form that reduces typographical errors and other mistakes.

## 2.3 Specialized Sample Introduction Techniques and Analysis

### 2.3.1 Aqueous Sample Introduction

Most of the FAAS and FAES systems use aqueous sample introduction through the nebulizer and into the burner head. This works well for samples that are already in the aqueous phase or can be digested in acid such as soil,

atmospheric particles, and tissue samples. All aqueous samples for FAAS and FAES contain some amount of strong acid, usually in the 1 to 5 percent. This acid acts to keep the metal analytes in the dissolved phase and to avoid adsorption of metal ions to sample container and instrument surfaces. FAAS and FAES operated under these conditions suffer from relatively poor detection limits that in some cases can be improved upon with specialized sample introduction techniques. These techniques, described below, are physical attachments to the basic AAS unit that may or may not replace the burner head and in some cases allow solid samples and high particulate containing samples to be analyzed. A few of the techniques allow the analysis of elements not commonly measured by FAAS or FAES.

### 2.3.2 Mercury Cold Vapor

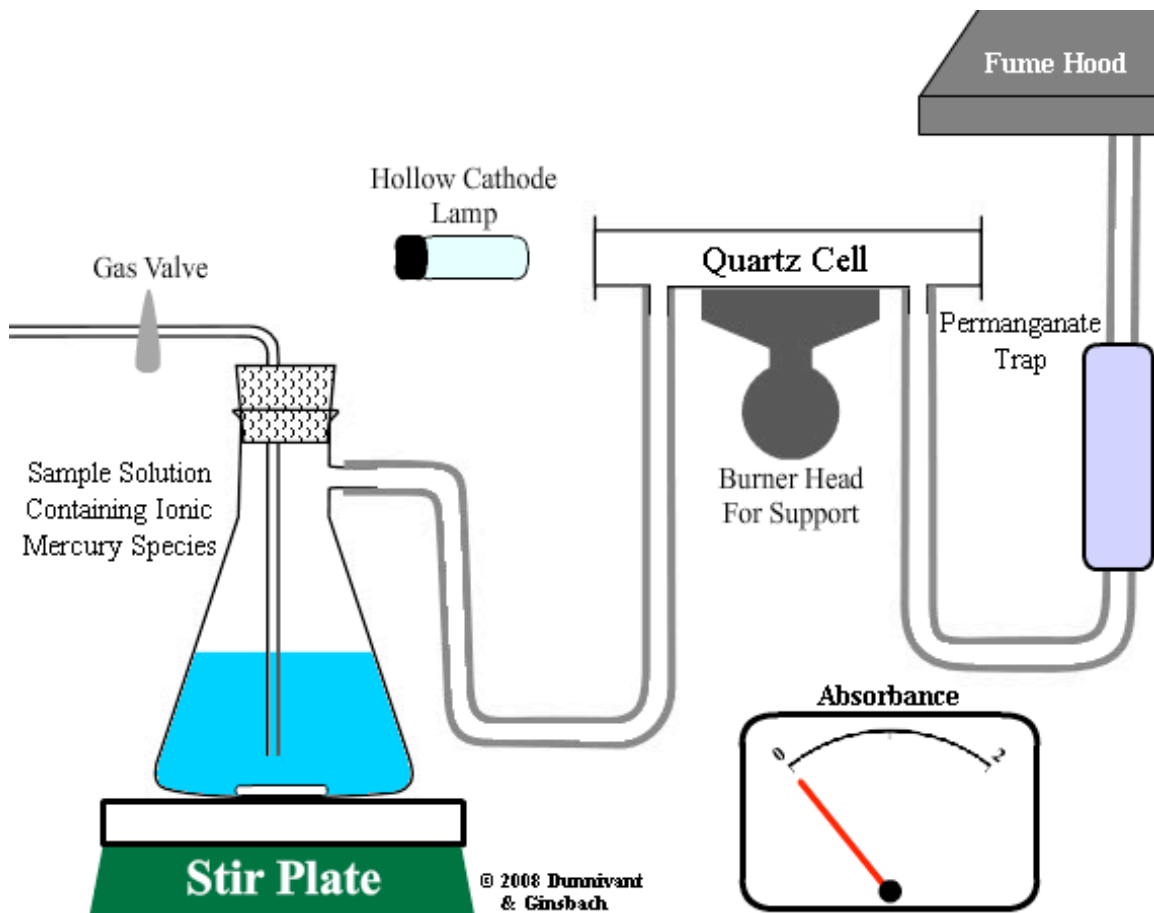
Inorganic and organic forms of mercury are ubiquitous in the environment, including water and food, and comes primarily from the burning of coal. As a result, it is necessary to detect the concentration of mercury to assess the danger caused by this toxin. Mercury is a neurotoxin and extremely small concentrations (part per billion or part per trillion) and can have detrimental effects due to bioaccumulation in the food chain (increases in concentration as one goes from one trophic level to the next). Several fish species, located in streams downwind from coal burning regions contain significant, and in some cases, dangerous concentrations of Hg. Flame AAS techniques only yield detection limits of approximately one part per million which is inadequate for environmental and food monitoring. The cold vapor technique described below yields detection limits in the parts per trillion range. Equal or even lower detection limits can be obtained by ICP-MS (the subject of Chapter 3 and 4) and atomic fluorescence techniques (a more advanced technique not included in this textbook).

An overview of the cold vapor system is shown in Animation 2.5 where an external glass vessel is used to generate elemental (and volatile) mercury that is

passed through a Pyrex/quartz cell placed on the standard burner head. No flame is needed to atomize the mercury, hence the name “cold” vapor technique.

A sample containing digested water, sediment, or tissue that contains cationic mercury ( $\text{Hg}^{2+}$ ) is added to the external glass vessel, which is then closed and purged with argon to remove any oxygen. Next,  $\text{SnCl}_2$  is added via a syringe to reduce  $\text{Hg}^{2+}$  to elemental Hg. The elemental Hg is stripped from the water solution and passes as a pulse of vapor through the sample cell. The instrument is operated in the absorption mode; a hollow cathode Hg source lamp provides a specific wavelength to be absorbed by  $\text{Hg}_{(g)}$  in the cell. After detection, the mercury vapor passes through a potassium permanganate solution to convert the mercury vapor back to ionic mercury so that no mercury is released into the laboratory environment or into the natural atmosphere. All blanks, external standards, and samples must be analyzed in the same manner. A drawback to this method is that samples must be processed individually, without automation. For each new sample, the argon stream must be interrupted to allow addition of a new sample to the glass container, which must then be purged with argon.

The advantage of the technique is a three order of magnitude improvement in the detection limit. Disadvantages are labor costs associated with digestion and manual instrumental analysis. When numerous samples are routinely analyzed this technique has been replaced with ICP-AES (with a detection limit of 1 part per billion) and ICP-MS (with a detection limit of less than 10 parts per trillion). Cold vapor mercury analysis is still commonly used when mercury is the only metal of interest and economics does not support the purchase and maintenance of an ICP-MS system. The reader should review Animation 2.4 at this time.



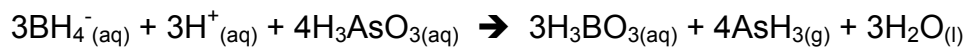
Animation 2.4 Illustration of a Cold Vapor Mercury Sample Introduction System.

### 2.3.3 Hydride Generation

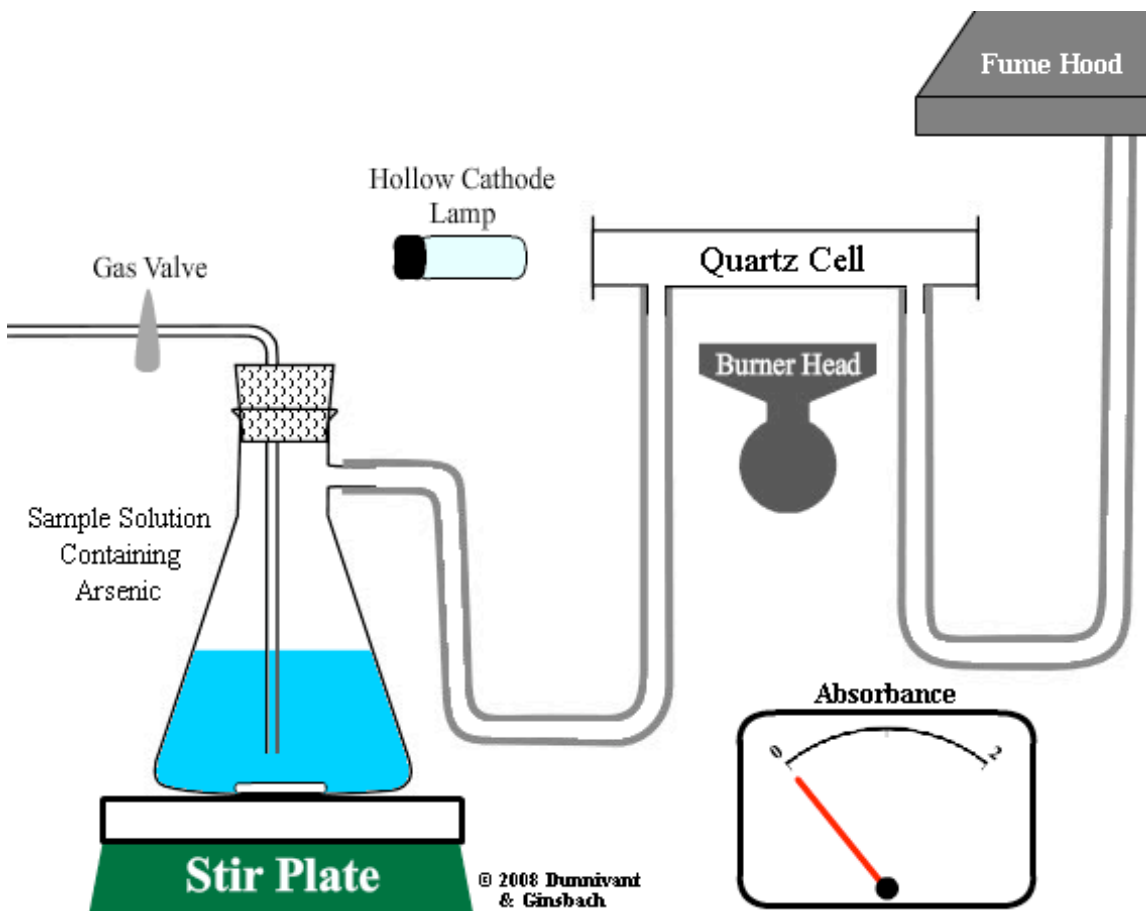
Another external attachment to a FAAS instrument is the hydride generation system that is used to analyze for arsenic (As), bismuth (Bi), mercury (Hg), antimony (Sb), selenium (Se), and tellurium (Te); some of these are notable toxins. This technique works in a similar manner to the cold vapor technique but sodium borohydride is used as the reducing agent to generate a volatile metal hydride complex. In addition, a flame is used to decompose the metal hydride. Again water, soil, and tissue samples must be digested to free the metal from organic and inorganic complexes and place it in its cationic state. The generated metal hydride is passed through the flame as a pulse input where it is degraded by heat to its gaseous elemental state. In this state the metal will absorb the

source radiation (again from a HCL) and the absorbance reading is directly proportional to the concentration of metal in the sample. Instrumental calibration and data processing is identical to the cold vapor mercury technique.

An example reaction that occurs in the reaction vessel for As is shown below



A video illustration of this technique can be viewed in Animation 2.5. As with the cold vapor technique the advantage is an improved detection limit, with the disadvantage of high labor costs associated with digestion and individual and manual instrumental analysis.



Animation 2.5 Illustration of a Hydride Generation Sample Introduction System.

#### 2.3.4 Electrothermal Vaporization (Graphite Furnace Atomic Absorption, GFAA)

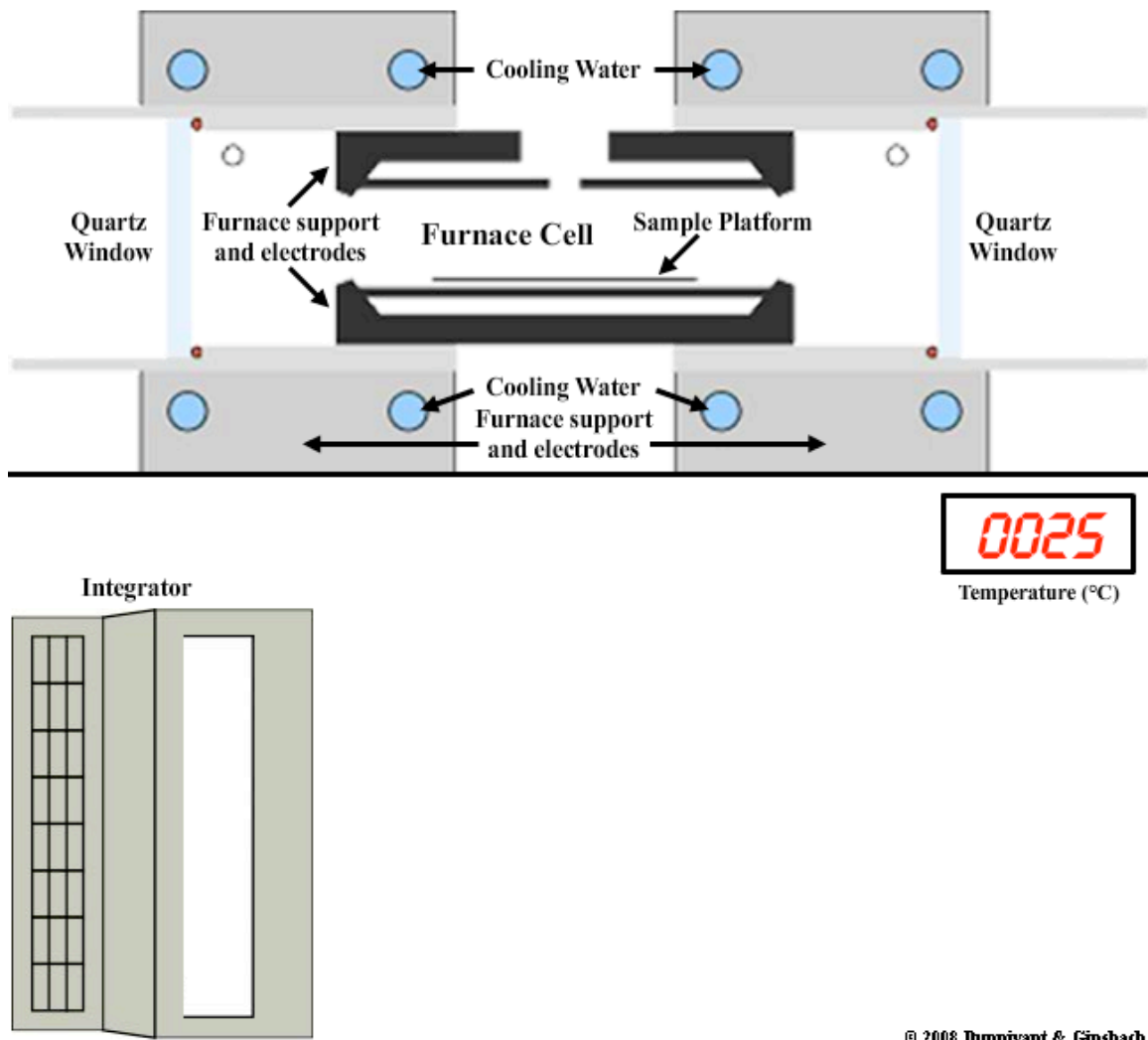
The graphite furnace, formally known as an electrothermal vaporization unit, uses a typical FAAS unit but replaces the burner head with a furnace system. No flame is used in the operation of this system; instead the metal in the sample is atomized by heating the cell with electrical resistance to temperatures not obtainable in flame systems. The heart of the system is illustrated in Animation 2.6. All systems use an automatic sampler to ensure reproducible results between replicate analyses. In GFAA, samples are usually digested (in acid) to assure homogeneity of the injected solution. A sample is placed into the graphite furnace cell through a small hole in the side. Cells range in size depending on the brand of the instrument but are usually about the diameter of a standard writing pencil (~ 0.5 cm) and 2 to 3 cm in length. Argon gas is passed through the cell to pass vapor and analytes into the radiant beam and the furnace and sample are then cycled through a three-step heating process. First, the water is driven off by resistance heating at 107 °C (which partially blocks the beam of the HCL source but this is not recorded). Next, the sample is “ashed” at 480 °C to degrade any organic material in the sample (again this absorbance signal reduction is not recorded). Finally, the cell is rapidly heated to 2000 °C where the analytes are placed in their volatile elemental state where they absorb radiant light from the Hollow Cathode Lamp; this signal is recorded. The system is then prepared for another run by heating the cell to 2500 °C to remove excess material before cooling the chamber with tap water back to room temperature. Then another standard or sample can be added and the process is repeated.

One obvious advantage of this system over the cold vapor and hydride technique is automation that reduces the cost of analysis. Another advantage of the GFAA technique over FAAS or FAES is the improvement in detection limits,



typically in the low parts per billion or high parts per trillion ranges. Most of the elements that are analyzed by FAAS can be analyzed by GFAA but high background concentrations of a few rare earth and alkaline earth elements in the graphite tubes limit their detection limits.

An illustration of sample introduction and the heating steps is given in Animation 2.6.



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Animation 2.6 Illustration of a Graphite Furnace Sample Introduction System.

The Zeeman Effect (Correction): In the graphite furnace samples containing high amounts of solids and organic matter can be introduced which lead to high background levels and spectral interferences when these compounds are heated and degraded during the atomization step. These problems can be overcome by using a Zeeman correction calculation. The Zeeman Effect capitalizes on the observation that the absorption profile of an element is split into several polarized components in the presence of a strong magnetic field. When absorption measurements using radiation from a deuterium or mercury vapor lamp are taken with and without a magnetic field present in the reaction cell, the presence of spectral interferences can be corrected for (subtracted out) and this difference in signals is referred to as the “Zeeman background corrected” atomic absorption signal. The physics behind this process is beyond the scope of this text and it is only important to note that the Zeeman correction is available and used in most graphite furnace systems.

### 2.3.5 Glow-Discharge Atomization for Solid Samples

The glow-discharge device is a highly specialized sample introduction system since it is mostly used for electrically conductive samples, such as a piece of metal or semiconductors. Like the GFAA unit it is an attachment that replaces the burner head. A sample is placed in a low-pressure argon chamber where a potential is placed between the container and the sample. Excited argon atoms sputter atoms from the surface of the sample, similar to the operation of the hollow cathode lamps. Gaseous phase metal atoms rise into the path of the source radiation and absorb their characteristic wavelength. The largest advantage of the glow discharge technique is the direct analysis of solid samples.

Fluorescence: The above discussions have mostly focused on absorption and emission processes and instruments. Recent advances in atomic fluorescence spectrometry make this technique possible for a few elements

(mercury, arsenic, selenium, tellurium, antimony and bismuth). Again, fluorescence occurs when an electron is excited to a higher electronic state and decays by resonance, direct line, or stepwise fluorescence (refer to Section 1.2.2). Instrument components are similar to those discussed above and in the next chapter, but the key difference is that the source lamp is located at a 90° angle with respect to the detector in order to prevent the source radiation from being measured by the detector. Lamps used to excite electrons include hollow cathode lamps, electrode-less discharge lamps, lasers, plasmas, and xenon arc lamps. Atomizers include flames, plasmas, electrothermal atomizers, and glow discharge chambers; thus samples can be introduced as cold vapors, liquids, hydrides, and solids. Sub-parts per billion detection limits are obtainable from these instruments.

## 2.4 General Operation of FAAS and FAES Instruments

Basic sample preparation will be discussed in Chapter 6, the experimental section of this Etextbook. For most FAAS and FAES measurements aqueous samples are required. Once samples are prepared, which can take hours, the instrument is prepared for operation. Instrument setup usually requires:

- checking the fuel and oxidant gas pressures and flow rates
- turning on the instrument and lamp (and aligning it, and allowing the electronics to warm up and stabilize for at least ten minutes),
- checking the drainage system to ensure waste flow,
- lighting the flame and allow it to thermally stabilize for five to ten minutes,
- adjusting (“balancing”) the electronics (this is automatically preformed on most modern instruments)
- testing the stability of the signal,
- loading the method and creating a sequence for the samples
- starting the sequence

## 2.5 Summary

FAAS and FAES dominated the market for decades but are slowly being replaced by ICP systems. Today, FAAS and FAES systems are limited to situations where only a few elements are analyzed occasionally. "Mass production" analyses in FAAS-FAES are most economical with automatic samplers but even then these techniques are being replaced by ICP-AES and ICP-MS, because of superior detection limits and other factors. These advanced techniques are the subject of the next two chapters.

## 2.6 Questions

Give the complete name of the following acronyms:

AES  
AAS  
FAAS  
FAES  
HCL  
PT  
PMT  
CCD  
LDA  
CTD  
GFAA

Draw and label double-beam flame atomic spectrometer.

What types of electromagnetic wavelengths do FAAS and FAES instruments use?

What is the difference between line and continuous spectrum sources?

Draw and explain how a hollow cathode lamp works.

What is the purpose of the chopper in an AAS or AES instrument?

How can an instrument perform both AAS and AES?

Explain the Bernoulli principle with respect to the FAAS burner head.

What is the optimum droplet size that makes it into and through the burner head and what factors influence this size?

What types of fuels and oxidants are used in FAAS and FAES?

Name and discuss all of the common sources of noise in the lamp and flame.

What is the purpose of a slit in the various locations in an instrument?

Draw a basic monochromator and explain how it works. What is its fundamental function?

What two components can result in dispersion in the monochromator?

Draw and explain how a phototube works.

Draw and explain how a photomultiplier tube works.

Contrast a phototube and a photomultiplier tube.

What is a dynode?

What is the difference between a discrete and a continuous PMT?

What is a charge coupled device?

What is the difference between a forward and reverse bias in a CCD?

What is the elemental difference between the p-doped and n-doped areas of a diode.

What is a diode?

What is a linear diode array, how does it work, and what are its advantages?

Contrast a PMT and a LDA.

What is a charge transfer device (CTD) and why are they replacing PMTs?

Contrast a CTD and a PMT.

Why are charge injection devices (CIDs) not common in FAAS and FAES?

How are complementary metal oxide semiconductors (CMOS) detectors superior to CCDs?

What are the sources of noise in detectors?

Explain how the signal to noise ratio used and why it is important.

How have computers changed FAAS and FAES instruments?

Draw and explain how the mercury cold vapor technique works.

Draw and explain how the hydride generation unit works in FAAS. What elements is it used to analyze?

Explain how a Electrothermal Vaporization (Graphite Furnace Atomic Absorption, GFAA) works.

How is the GFAA unit superior to the FAAS or FAES instruments?

How does the glow-discharge unit work? In what industry is it mostly used?