

## CHAPTER 4

### Inductively Coupled Plasma—Atomic Emission Spectrometry

#### 4.1 Introduction and History

Greenfield et al. developed plasma-based instruments in the mid 1960s about the same time flame-based instruments such as FAAS and FAES (Chapter 2) became prominent (*Analyst*, 89, 713-720, 1964). These first plasma-based instruments used direct current (DC) and microwave-induced (MI) systems to generate the plasma. Interference effects and plasma instability limited the utility of plasma instruments during analysis; consequently flame-based spectrometry instruments (such as FAAS) dominated the analytical market for metals analysis and remain effective today.

The limitations of the first plasma instruments were overcome by utilizing an inductively coupled plasma (ICP) instead of DC or MI generated plasma. ICP optical systems became popular in the 1980s due to their decreased cost, lower time investment during analysis, and labor saving advantages. FAAS instruments require a unique radiation source (lamp) for the approximately 35 elements they can measure. Because the lamp must be changed between each element of interest, FAAS (and FAES) techniques analyze a single element at a time and are unable to easily analyze metalloids. ICP optical systems, by contrast, can analyze about 60 different elements at the same time with a single source (the plasma). The most common instruments today are inductively coupled plasma—atomic emission spectrometers (ICP-AES) and inductively coupled plasma—mass spectrometers (ICP-MS). ICP-AES will be discussed in this chapter while ICP-MS will be the subject of the next chapter.

#### 4.2 Atomic Emission Spectrometry Theory

The operation of an ICP-AES system relies upon the same interaction of molecules with electromagnetic radiation that was presented in Chapter 1. The

two emission systems, FAES and ICP-AES, differ in the way atomic species are created and excited. Because of the relatively low temperatures (~2000-2500 C) in a flame-based system, not all of the atoms or elements present in the sample are excited, particularly if they exist in a polyatomic compound. Some elements readily form non-emitting and refractory oxides that result in an underestimation of their concentration. In plasma-based systems the temperature is considerably hotter (~10 000 K for Ar ICP) that results in more effective excitation of atoms (generally greater than 90%) of approximately 60 elements including some nonmetals. This intense heat prevents polyatomic species from forming, thus increasing the detection limits for many elements. Atoms are excited, and in many cases ionized, by the intense heat of the plasma, and the emission of a photon occurs via resonance fluorescence (normal valence electron relaxation by photon emission). While plasma-based systems eliminate many problems, they are not free of interferences due to the excitation and subsequent emission of spectral lines for every element in the sample as well as the Ar added to facilitate plasma generation. The spectral overlay that results from these possible emissions is overcome in modern instruments with specialized sequential monochromators (Section 4.4.4). ICP-AES, compared to FAAS/FAES, offers high selectivity between elements, high sensitivity, a large dynamic range, especially as compared to FAAS that is limited by Beer's law, lower detection limits, multi-element detection, and fewer matrix interferences.

### 4.3 Components of an Inductively Coupled Plasma—Atomic Emission Spectrometry System (ICP-AES)

#### 4.3.1 Overview:

An ICP-AES system can be divided up into two basic parts; the inductively coupled plasma source and the atomic emission spectrometry detector. Figure 4.1 shows the common components of an ICP-AES system from the late 1980s to the 1990s. The inductively coupled plasma source has mostly been

unchanged since its invention with the exception of innovation in monochromator type, which enables greater suppression of interference phenomena.

Modifications of this common system will be explained in the following sections.

Sample solutions include digested soil or other solid material or natural water. Typically the sample solution is acidified up to 2-3% in  $\text{HNO}_3$  to prevent adsorption of metals onto polypropylene sample bottle or onto instrument tubing or glassware prior to introduction into the plasma. In Figure 3-1, the sample is introduced to the nebulizer chamber via a peristaltic pump and tygon tubing attached to an automatic sampler. A peristaltic pump operates by sequentially compressing flexible tubing with evenly spaced and rotating rollers that pull/push the liquid through the system. The rate of sample introduction into the plasma changes as the rotation rate of the peristaltic rollers increases or decreases. Flow of sample and Ar gas through the small aperture of the nebulizer creates very small droplets that form a mist of  $\mu\text{m}$ -sized particles in the nebulizer chamber. Larger sample droplets collect on the chamber walls and are removed through a drain, while smaller particles travel with the Ar flow and enter the torch. Evaporation, atomization, and excitations/ionizations occur in the plasma at temperatures reaching 10,000 K. Ar not related to the sample is also excited and ionized because this gas both carries the sample aerosol and confines the location of the plasma to prevent damage to the rest of the instrument. As the excited/ionized atoms leave the hot portion of the plasma, excited valence electrons relax and emit a photon characteristic of the electron transition. This photon is specific to the element but does not yield any information about the isotopic state of the element, unlike in mass spectrometry (Chapter 5). Visible and UV radiation emitted from the sample constituents enters the monochromator through a small slit where the wavelengths are separated by grating(s) and/or prism(s) before being captured and measured by a wide variety of detectors.

Because spectral interferences may still occur, the choice and configuration of the monochromators in the instrument is important and has been

the target of innovation. In Figure 4.1, the most common form of a monochromator (a Rowland circle) and detector (photomultiplier; PMT) is shown: The Rowland system utilizes a concave Echellette-style grating monochromator to separate the various emission lines and simultaneously focus individual wavelengths on to a series of slits, with each slit aligned to allow a specific wavelength of radiation to pass to a detector. The standard detector, a photomultiplier tube (PMT), was discussed in Section 2.2.9. Some systems use multiple PMTs at fixed locations to monitor each wavelength simultaneously (Figure 3-1) whereas other systems use a single PMT and move it to different locations to detect each wavelength. Data from these detectors are processed by a computer because multiple wavelengths are measured in an ICP-AES system at the same time.

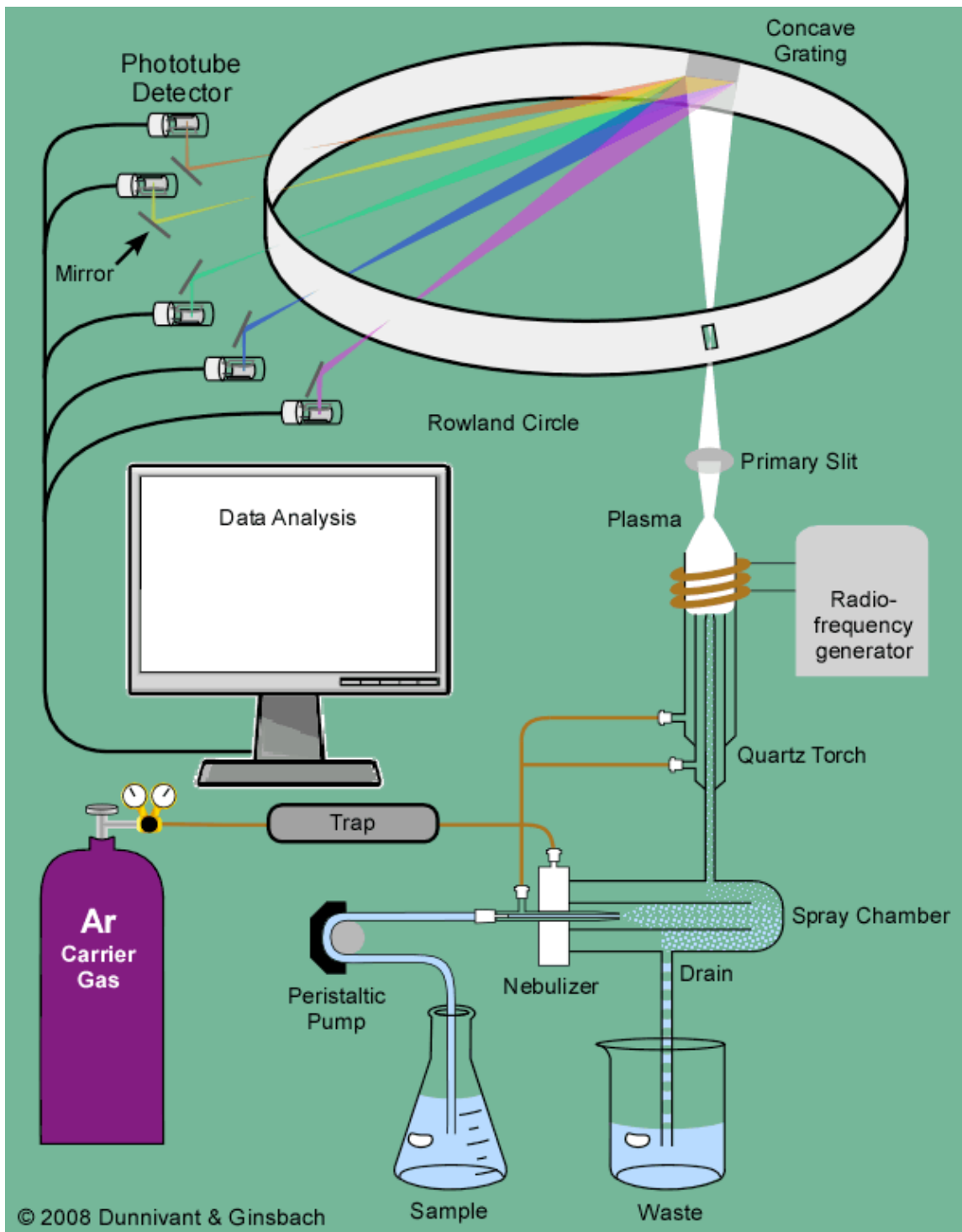


Figure 4.1. Overview of a Basic Inductively Coupled Plasma—Atomic Emission Spectrometry (ICP-AES) from the 1990s.

#### 4.3.2 Sample Introduction and Optimization

The predominate form of sample matrix in ICP-AES today is a liquid sample: acidified water or solids digested into aqueous forms. Given the automated nature of the ICP analysis, all modern systems are purchased with automatic samplers where a computer-controlled robotic sampling arm takes liquids from each sample via a peristaltic pump from plastic tubes located in specific locations in a sampling tray. Liquid samples are pumped into the nebulizer and sample chamber via a peristaltic pump as shown below. Then the samples pass through a nebulizer that creates a fine mist of liquid particles. Larger water droplets condense on the sides of the spray chamber and are removed via the drain (pumped out of the chamber also by the same peristaltic pump) while finer water droplets move with the argon flow and enter the plasma. Nebulizers help ensure that the sample enters into the plasma at a uniform flow rate and specific droplet size. Droplets that are great than 5  $\mu\text{m}$  in diameter are likely to interfere with plasma stability.

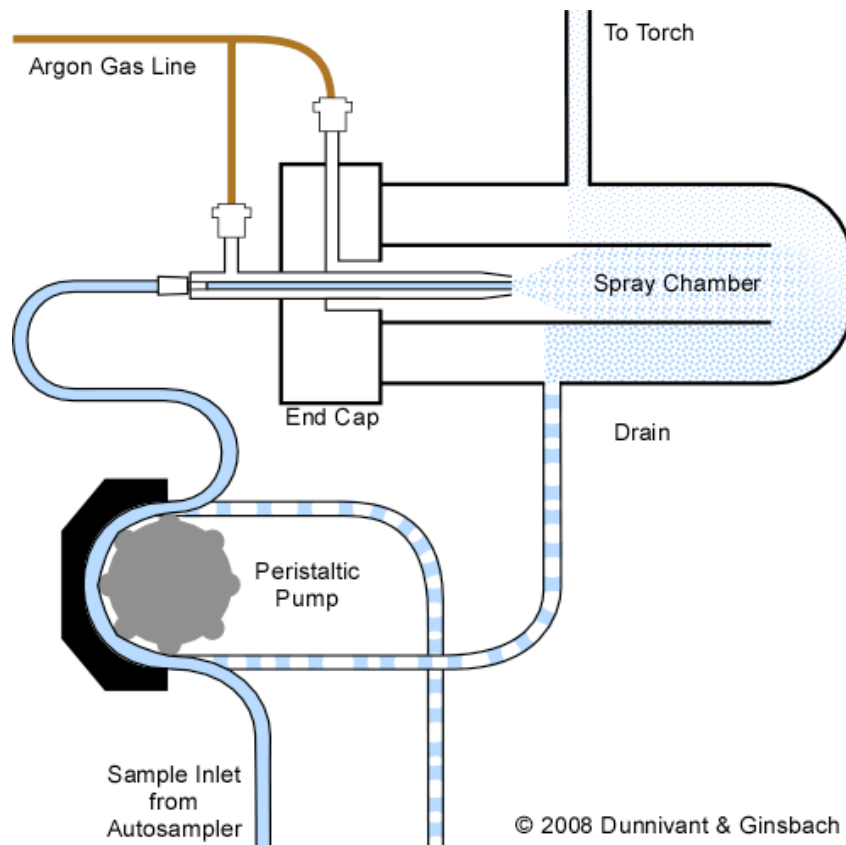
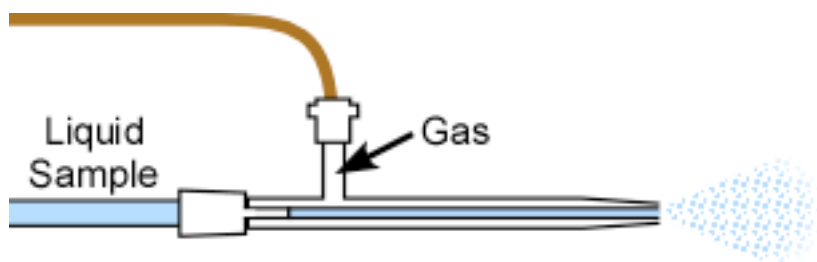


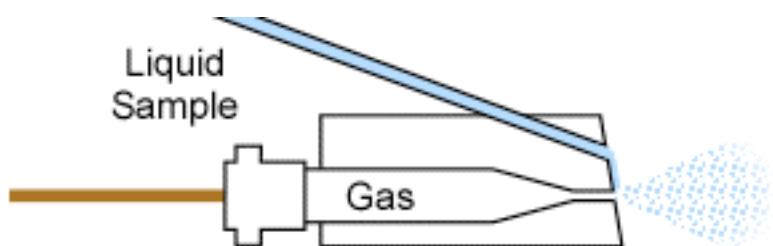
Figure 4.2. An Overview of Sample Introduction and the Nebulizer Chamber.  
(The nebulizer shown here is a pneumatic style, described below.)

While there are numerous types of nebulizers for a variety of specific applications, the three most commonly types are the (1) pneumatic, (2) ultrasonic, and (3) grid. Because argon is used in generating the plasma (discussed below) it is most often used as the gas in these various nebulizers, but other gases can be used. The most common pneumatic nebulizer for samples containing low concentrations of total dissolved solids is the concentric nebulizer shown in Figure 4.3, but higher suspended solids and dissolved solids samples are commonly introduced to the plasma via the Babington nebulizer.



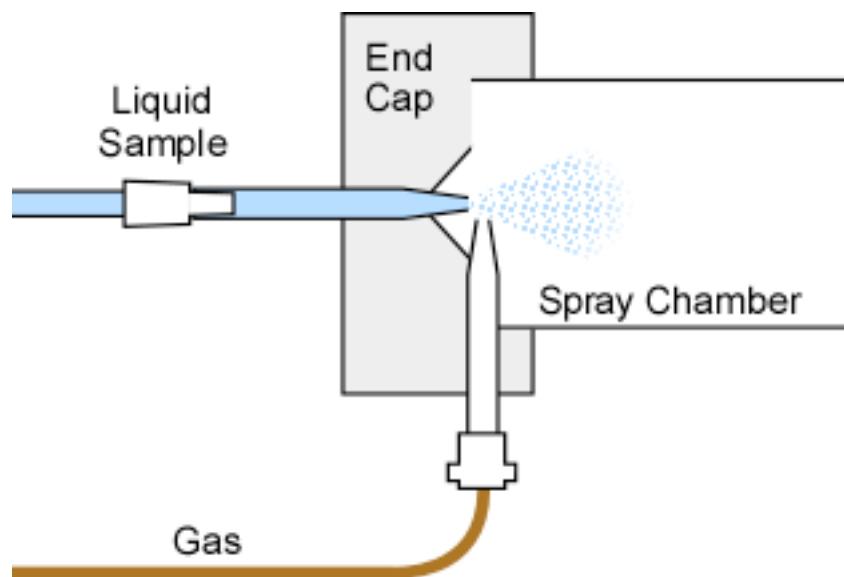
© 2008 Dunnivant & Ginsbach

Figure 4.3. Diagram of a Pneumatic Concentric Nebulizer.



© 2008 Dunnivant & Ginsbach

Figure 4.4. Diagram of a Pneumatic Babington Nebulizer.



© 2008 Dunnivant & Ginsbach

Figure 4.5. Diagram of a Pneumatic Cross-Flow Nebulizer.

Ultrasonic nebulizers are used to provide more sample delivery to the plasma and thus improve detection limits. An ultrasonic generator surface, usually a piezoelectric crystal that rapidly vibrates to generate sonic energy, is used to create extremely fine droplets that, at low flow rates, are completely transferred to the plasma (unlike considerably lower efficiencies from pneumatic nebulizers). Grid nebulizers create a fine mist by placing a grid in front of the argon flow. The liquid sample is allowed to flow down the grid and as argon passes through the grid it creates fine droplets. Again, the most common commercially available nebulizers use the pneumatic design.

ICP systems have a few sample requirements or limitations. Micrometer-sized particles must be removed by filtration or centrifuge or dissolved prior to introduction to a sample vial because the particles can easily clog the tip of the nebulizer. A clogged tip will not be automatically detected by the instrument, but will be detected by a trained operator by the absence of any sample, internal standard, or standard analyte concentrations in the final.



Another limitation of the nebulizer is the presence of high total dissolved solids (TDS) that will eventually cause the accumulation of solids in the tip of the nebulizer, as well as in the sample chamber and on the sampler cones located just after the plasma (in ICP-MS instruments only). Most ICP instruments limit the sample TDS level to approximately 0.1 to 0.2 percent salts by weight. Higher salt contents can enhance atomization and ionization of some elements and suppress or interfere with others (Walsh, 1997). Likewise, the acid concentration of liquids entering the plasma should be limited to approximately two to three percent for nitric and hydrochloric acid. Rarely hydrofluoric acid may be used if a particularly refractory element is of interest, but then the acid concentrations are less than 0.5% because it will degrade the quartz torch with time. Some samples, such as food-based beverages or plant extracts, can contain high concentrations of organic matter. It is best to oxidize this organic matter in an acid or peroxide digestion prior to analysis since carbon will rapidly accumulate on the components of the instrument if high organic matter containing samples are directly injected into the plasma. This carbon can reduce sample flow and capture elements and ions as the carbon builds up, specifically at the cone apertures that facilitate the transition from ambient pressure in the plasma region to the high vacuum detector region (in ICP-MS systems). When a portion of a carbon plaque drops back into the analytical stream, an anomalously high, and false, measurement can occur.

Other forms of sample introduction are used but are not as common as liquid injection. These include (1) direct insertion of 10-30 mg of sample on a graphite probe into the plasma via the normal nebulizer entry port, (2) the injection of the effluent from chromatographic separation systems, especially from high performance liquid chromatography (HPLC), supercritical chromatography, and ion chromatography (IC) units where compounds containing elemental analytes of interest are first separated by chromatography and then introduced into the plasma for elemental analysis, (3) where the cold vapor techniques described in Section 3.4 for mercury analysis is connected to

the plasma inlet via the nebulizer port, and (4) where the hydride generation system from Section 3.4 for selected metals can also be connected to the nebulizer port.

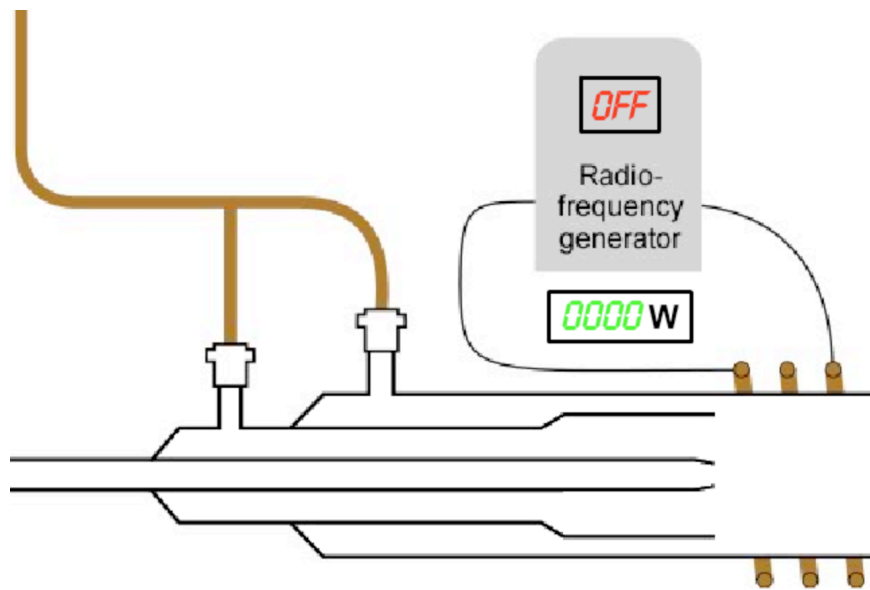
#### 4.3.3 The Inductively Coupled Plasma Torch

The torch unit of an ICP is used to create and sustain a plasma. A plasma is an electrically conducting gaseous mixture containing enough cations and electrons (though the plasma has a neutral charge overall) to maintain the conductance. One common example of a simple plasma is a regular flame which will conduct an electrical current across it; cations and electrons are created upon ignition of the fuel and travel upward in the flame until they are cooled above the flame. Another common plasma is used in scanning electron microscopy (SEM) where a sample is coated with graphite or a metal in a vacuum chamber in order to make the surface conductive (a standard requirement for obtaining high quality images). DC arc and microwave plasmas can also be used to generate plasmas, but for purposes of metal analysis, the inductively coupled plasma system described below is most important. The purpose of the torch is to (1) evaporate the solvent (usually water) from the analyte salts, (2) atomize the atoms in the salt (break the ionic bonds and form gaseous state atoms), and (3) excite or ionize the atoms. In the case of ICP-AES, only excitation is needed as in FAES but given the extreme temperatures (up to 10 000 K) of the argon plasma used in modern ICP systems, the excitation of atoms is virtually complete for most elements. (Chapter 4 describes how the ICP-MS capitalizes on the efficient ionization of atoms in the plasma.) A modern torch system is illustrated in Animations 4.1 and 4.2. The torch described here is composed of three concentric quartz tubes. The samples and the argon gas used to aspirate it pass through the center tube. The plasma generating gas (argon) passes through the middle tube, and the argon passing through the outer tube is used to cool the quartz torch.

The plasma is sustained by a radio-frequency generator that creates an oscillating magnetic field around the torch that results in ohmic (inductive) heating of the charged gases at the end of the torch. Ohmic heating occurs when an electrical current is passed through a conductor, that in turn, creates more heat. Three types of radio-frequency generators have been used. Older types are based on piezoelectric crystal oscillators and “free-running” generators in which the oscillation is set according to the combinations of the components of the circuit; examples include the Armstrong, Hartley, Colpitts, and tuned-anode-tuned gate oscillator electronic circuits. Most modern analytical ICP systems use solid-state semiconductor generators where the circuit consists of (1) a capacitor used to store a high electrical charge (thus requiring the 220-240 V electrical power requirements) and (2) an inductor coil to deliver the oscillating current to the torch and generate the magnetic field around the torch. The capacitor is hidden from view in ICP systems and buried in the electronics of the instrument. The inductor coil is visible and is the approximately 3-mm hollow copper coil wrapped three times around the end of the torch. The capacitor responsible for generating the plasma from argon gas, oscillates an electrical field at a rate between approximately 27 and 41 MHz (a frequency regulated by the FCC) and through induction creates a magnetic field in the plasma. The intensity of the frequency, measured in Watts, is sufficient to promote the valence electrons in some of the Ar atoms but not ionize them sufficiently to initiate or sustain a plasma. The creation of plasma occurs when a spark (from a Tesla coil; basically an automatic gas grill lighter) introduces free electrons at the end of the torch when the electrical field is being oscillated at a specific frequency by a RF generator. The seed electrons from the Tesla coil oscillate in an angular path and periodically collide with argon gas atoms and ionize them, releasing more electrons. Due to their kinetic energy and collisions with other atoms a large amount of heat is generated, enough to generate and sustain a plasma at temperatures up to 10,000 K. In terms of an electrical analogy, the term “inductively coupled” in ICP is a result of the coupling of the induction coil and the electrons. The copper induction coil serves as the “primary winding” of the radio-

frequency transformer and the “secondary winding” is the oscillating electrons and cations in the plasma; the two “windings” are thus coupled together because the second winding depends on the presence of the first. The RF generator also contains a feed back loop where the interaction of the electronic/magnetic field in the capacitor/induction coil is monitored. If the flow rate of argon gas is too low or if small amounts of O<sub>2</sub> or high amounts of water vapor are present in the torch during the initiation of the plasma, the RF generator will sense their presence by a change in the feedback between the oscillation and the RF generator. When this happens, the RF generator shuts down to protect the electronics in the system from overheating. Thus, atmospheric O<sub>2</sub> cannot be present in the Ar and the flow rate of nebulizer sample (water) must also be controlled to successfully light the torch. The process of lighting the plasma is visualized in Animation 4.1.

In this animation the argon is turned on and the pressures are allowed to equilibrate without the introduction of any sample or blank solutions to the nebulizer. The radiofrequency generator then ramps the wattage through a series of cycles. A typical ramp cycle begins by turning the RF generator to 200 Watts. Subsequently the electronics go through a preliminary check that adjusts the electronics and minimizes the resistance between the RF generator and the induction coil. Next the RF wattage is ramped to 900 W where excitation of valence electrons in some Ar atoms occurs and the Tesla coil initiates the excitation and ionization of Ar atoms and the plasma is lit. The circulation of electrons and Ar cations in close association results in ohmic heating that generates more electrons, collisions between Ar atoms, and an increase in temperature. The wattage is then increased to 1200 and the resistance is minimized again via electronic adjustments. Finally the wattage is adjusted to the suggested energy level for the elements of interest; this is usually between 1250 and 1550 W. Please review Animation 4.1 on the book’s web site at this time.



Animation 4.1. Animation of the Gas Flow, RF Wattage Adjustment, and Lighting of the Plasma Torch Commonly used in ICP Systems. See the book's web site for the actual animation.

If the region of ohmic heating is not controlled, the plasma would continue to heat until it melted the quartz torch (and the other components of the ICP spectrometer). The torch is cooled in two ways, the first is by the tangential introduction of relatively large volumes of argon gas through the outer tube of the torch. This argon flow spirals around the middle tube resulting in uniform cooling. Furthermore cooled water flows through the copper induction coil of the RF generator that is wrapped around the end of the torch. These combined cooling systems promote an equilibrium maximum temperature of approximately 10 000 K in the hottest portion of the plasma. The portion of the plasma that ICP-AES measurements are concerned with is about 5000-6000 K and is located in cone-shaped region outside the quartz torch.

After successful ignition of the torch, samples are introduced into the system through the nebulizer (Animation 4.2). Upon entry into the plasma, the solvent evaporate and salts form. Then, these compounds decompose as they move farther into the hotter portions of the plasma. Next, the valence electrons on the analyte atoms are excited (for ICP-AES measurements) or completely removed (ionized for ICP-MS measurements). The intense heat that sample molecules encounter in the plasma is sufficient to decompose most refractory compounds, thus only atoms or atomic ions are present in the plasma (Section 4.4). This heat also causes complete excitation of atoms and leads to higher detection limits, compared to FAES where the extent of excitation is element- and flame temperature-dependent. In ICP-AES, as the atoms exit the plasma and cool to approximately 6000 K, they relax and emit a characteristic photon that enters one of the monochromator/detector systems described in the next section. In ICP-MS (Chapter 4), the plasma enters a vacuum chamber where the cations are separated by a mass filter (mass analyzer) and detected by a specialized photomultiplier tube. An illustration of the drying, atomization, and excitation and ionization is shown in Animation 4.2. Please refer to the book's web site for Animation 4.2



Animation 4.2. Animation of Sample Introduction and the Subsequent Reactions in the Torch of an ICP System. Note that this animation is a simplistic illustration of a complex process and water molecules do not actually remain intact at 10,000 °K. Charge transfer to the cations actually occurs due to Rayleigh explosion.

The consumption rate of Ar gas is an important issue and accounts for most of the operational costs of an ICP. Older systems can use up to 20 L/minute, while modern systems have reduced the flow to below 10 L/minute. Systems are being designed that are portable and use far smaller flow rates of Ar gas. Many laboratories use cryogenic sources of Ar to reduce operational costs. Current prices for *liquid* Ar (equivalent to approximately 5000 cubic feet at STP) are approximately \$325, whereas the cost of three T-size cylinders of *gaseous* Ar (equivalent to approximately 334 cubic feet at STP) is approximately \$420. Thus, use of a cryogenic tank is far more economical than individual gas cylinders. Gases generated from a cryogenic tank are often more pure than those obtained from a standard T-sized gas cylinder.

Around 2005, a new version of ICP-AES was introduced to the market based on a microwave-induced N<sub>2</sub> plasma. A major advantage of this system is that it uses atmospheric N<sub>2</sub> to generate the plasma and greatly saves on cryogen costs by using a relatively inexpensive, built in nitrogen generator. One slight limitation of the system is the lower plasma temperature, ~5,000K, that results in relatively lower detection limits, comparable to FAAS detection limits, but lower than Ar-based ICP-AES systems.

#### 4.3.4 Separation and Detection

After the atoms are excited or ionized in the plasma, they exit the high temperature region and electronically relax. This results in the emission of at least one element-specific photon available for detection. The first choice to be

made by the analyst is the position of the monochromator entrance relative to the plasma source. Two choices are available, axial and radial alignment. A radial design allows photons to move from the side of the plasma (at the end of the torch) to the entrance slit while an axial design gives higher intensities (and better detection limits) since the photons come from the center and end of the plasma. Thus, depending on the concentration of analytes in a given sample, the analyst may choose to monitor the emissions from the radial angle for higher concentrations; this avoids burning out the detector, which is costly to replace. Or the analyst may choose to use the axial monochromator alignment for lower concentration samples. Changing the angle of observation can potentially avoid additional sample preparation such as dilutions. Many brands of instruments allow a selection between radial and axial monitoring.

Three broad categories of detection are available for analyzing the emitted photons: sequential, simultaneous multi-channel, and Fourier transform systems. In the first two, all wavelengths enter a monochromator where they are dispersed by prisms and/or grating monochromators and are then transmitted to the detector (most commonly the PMT presented in Animation 3.4, or a CCD presented in Figure 3.9). Fourier transform systems produce spectral separations by capitalizing on constructive interference techniques as first developed for Michelson's interferometer in 1881. In Fourier transform systems, no slits or monochromators are required, and this creates better detector limits because more intense radiation reaches the detector. Fourier transform systems also have higher spectral resolution (and thus have fewer spectral interferences) and can simultaneously monitor all wavelengths for longer times. This text will only cover sequential and simultaneous multi-channel systems that use monochromators because Fourier transform systems extend past the basic ICP instrumentation goal of this eTextbook and are considered "higher end" systems.

The first ICP-AES systems used a sequential monochromator to separate the analyte-emitted photons by wavelength before detecting them with a single



detector. This approach is analogous to the FAES system where only one element could be analyzed at a time. In a sequential system, if a sample needed to be analyzed for multiple elements, the grating system was rotated to direct the appropriate wavelength to the exit slit of the monochromator and into a PMT (described in Section 3.2.9). While ICP-AES provided superior detection limits compared to FAES instruments, it was just as slow and labor intensive as FAES.

Simultaneous multi-channel systems rapidly became economical as component production costs decreased and as labor costs have increased with time. In these systems, multiple elements can be detected at the same time using one of two designs. One way is to use a standard grating monochromator that separates the photons based on wavelength and directs the photons of interest to specific exit slits. Then, a single detector was rapidly moved from one slit to the other to analyze photons of various wavelengths. This type of system is shown Figure 4.6. Another way to accomplish multiple element detection is by placing an individual detector, again usually a PMT, at each exit slit. Such a system, the Rowland circle, was shown in Figure 4.1 and is shown again here as Figure 4.7. The Rowland design increases the upfront cost of an instrument and the running cost as PMT are replaced but this design significantly decreases the analysis time.

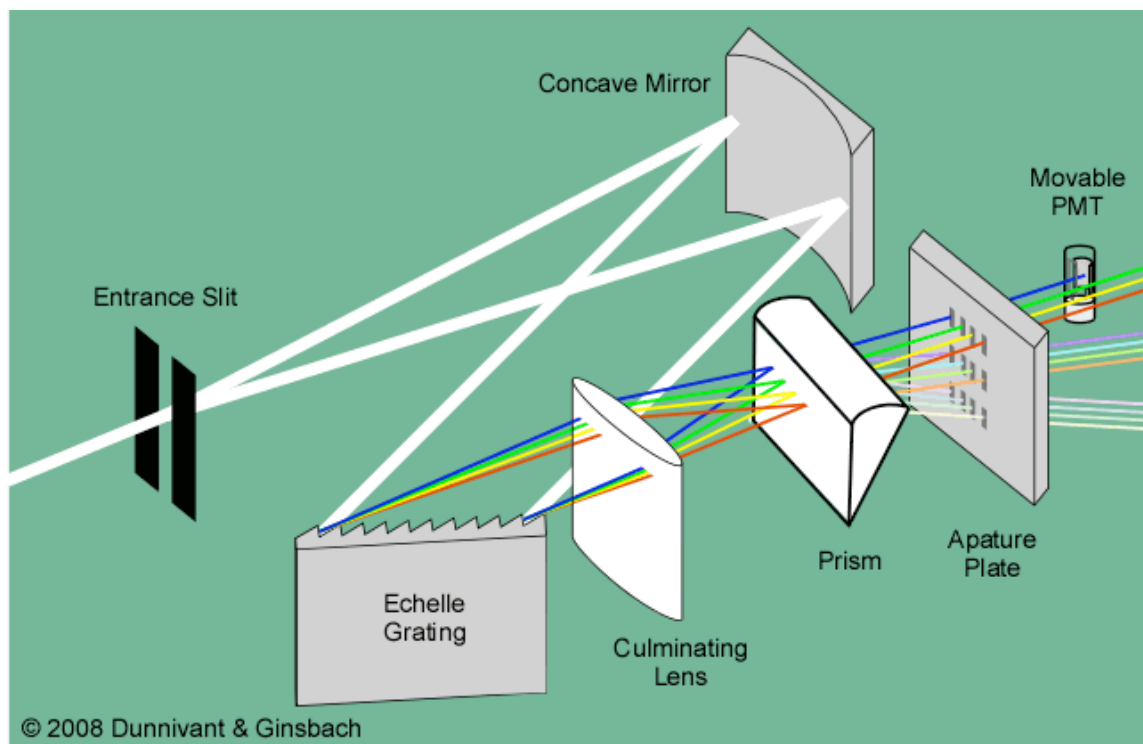


Figure 4.6. A Single Detector (sequential type monochromator) ICP-AES System.

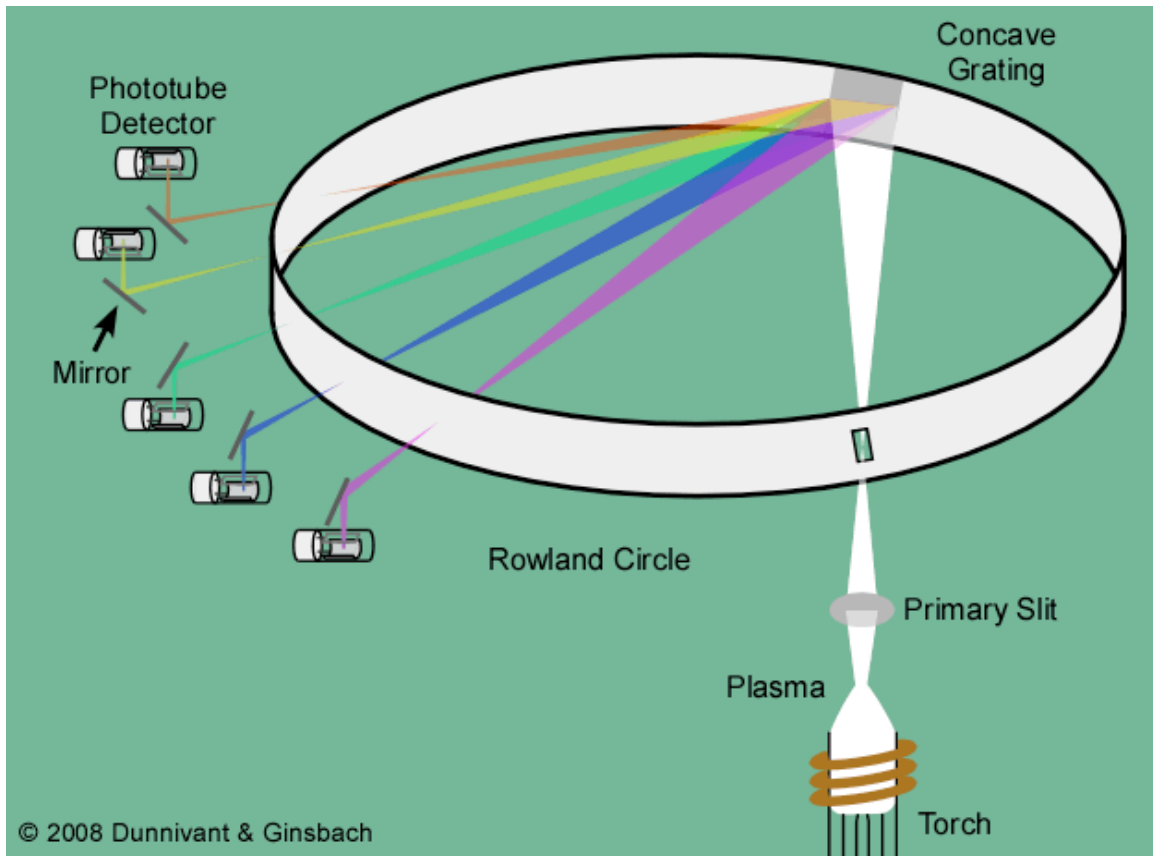


Figure 4.7. A Rowland Circle ICP-AES System.

More recent advances, use a combination of two monochromators (one prism and one Echelle grating, or one conventional grating monochromator and one Echelle grating), remove the exit slit, and place a multiple element detection system, such as a charge coupled device (CCD described in Section 3.29, Figure 3.9) or charge injection device (CID described in Section 3.29, Figure 3.9) in the path of the separated wavelengths (refer to Figure 4.8).

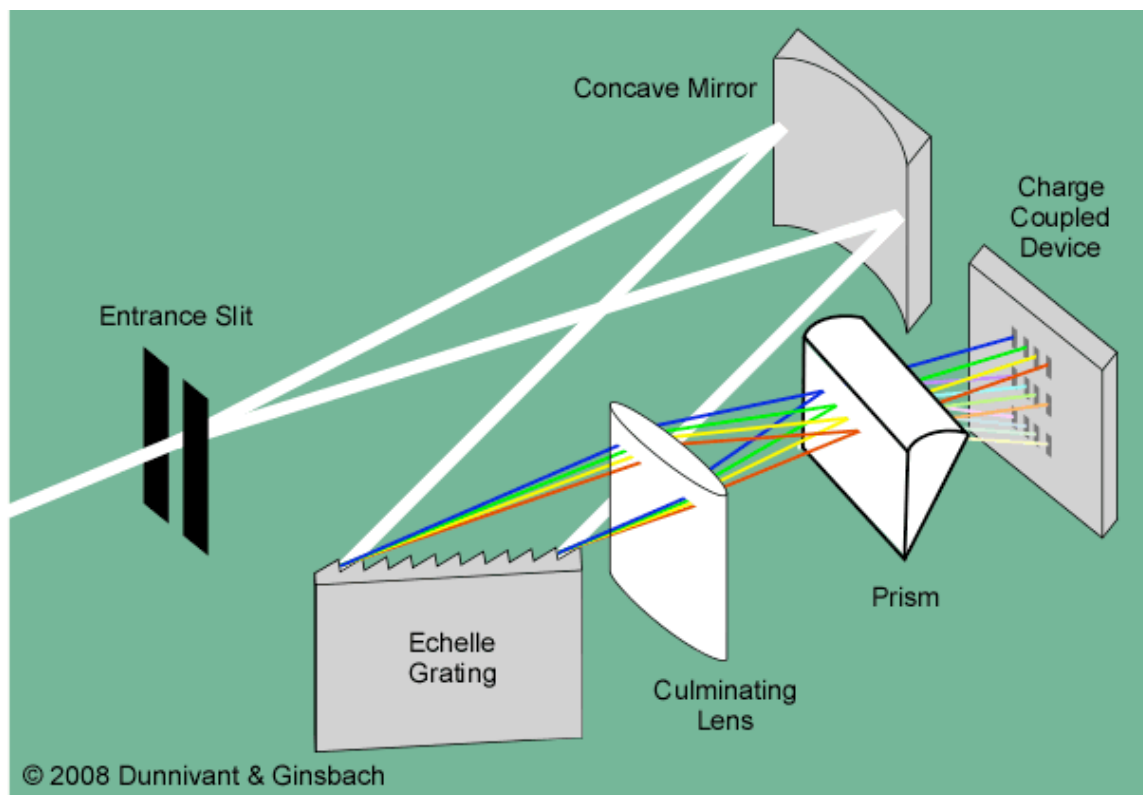


Figure 4.8. A Multiple Monochromator ICP-AES Instrument.

Some instruments use one detector for UV wavelengths and another for visible wavelengths. There are a variety of designs for these latter systems illustrated below. These more advanced instruments have an increased cost but are more economical recently due to decrease in the production costs of CCDs and CIDs versus PMTs. They also significantly reduce the lab bench space requirements. Instruments such as the one in illustrated in Figure 4.9 (1) offer superior resolution compared to a Rowland circle due to the advance monochromator systems, (2) offer the immediate option to monitor secondary or greater diffraction that can be used in high concentration samples, (3) reduce the size of the instrument due to the reduced size of the detector(s), and (4) offer more inexpensive instruments as the cost of CCDs and CIDs become more economical.

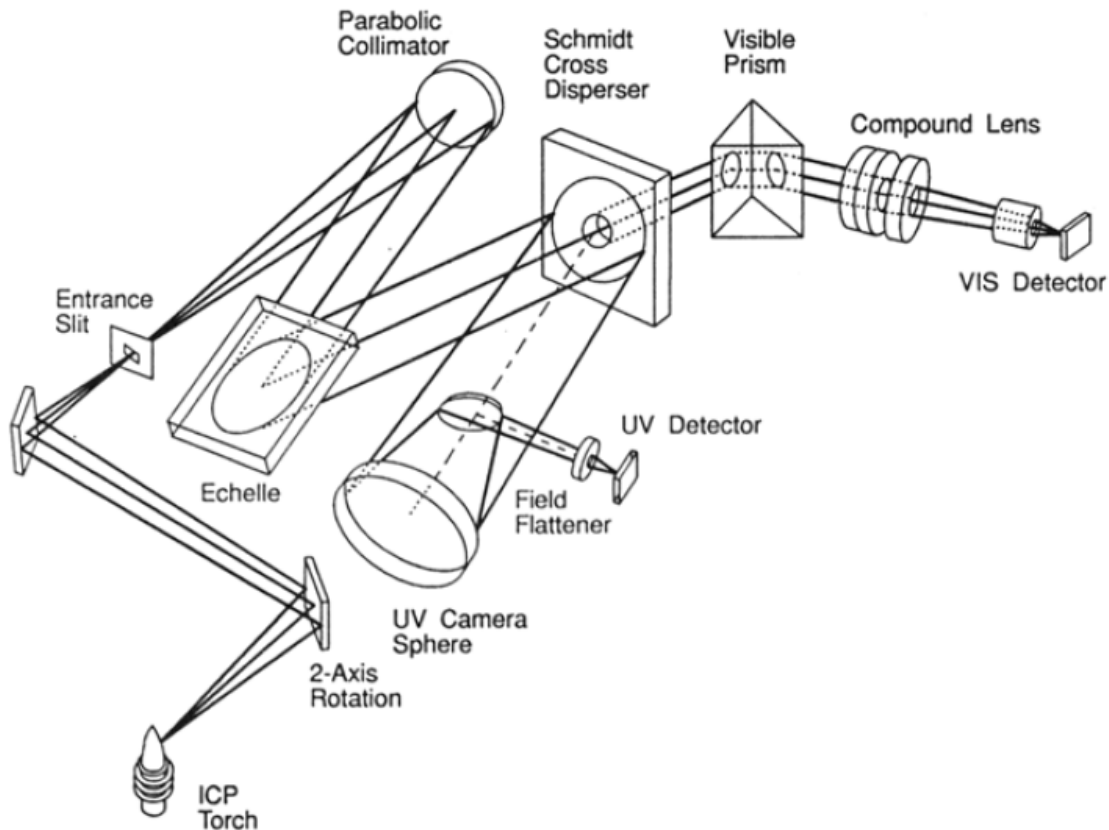


Figure 4.9. A Dual Echelle Grating – Prism Monochromator ICP with Dual CCD Detectors. From Barnard et al., *Anal. Chem.*, 1993, 65, 1231. Reprinted with permission from ACS.

#### 4.3.5 Data Collection

When single element detection was the goal of instrumentation, a simple chart recorder or digital display was sufficient for data collection. However, with the advances in ICP-AES technology today, computers are a necessity, not only to control the automatic sampler and the instrument control but also for data collection. Data collection systems are divided into a “method file” to run the instrument and “sequence file” to tell the instrument where a sample is in the sample tray, when to run it, and where to store the collected data file.

#### 4.4 Interferences:

ICP systems greatly reduce the number of interferences over those created in flame-based systems. Nebulizer, chemical, ionization, and spectral interferences are all present in ICP systems, but spectral interferences are most prominent. Nebulizer interferences (also known as matrix effects) can arise from physical and chemical differences between reference standards and samples, or between samples, such as the inconsistent presence of matrix salts and organic compounds or different viscosities and surface tension of the liquid. Each of these can be overcome by the use of standard addition calibration techniques discussed in Chapter 1, but at a significant increase in the cost of analysis (primarily due to labor costs). For low ionic strength samples, nebulizer interferences are less prominent. Chemical interferences are common in FAAS and FAES but are less common or practically nonexistent in ICP-AES due to the relatively high temperature of the plasma, long residence time in the plasma, and inert atmosphere of the Ar plasma. Ionization interferences, in direct arc- and microwave-produced plasmas, usually only occur for easily ionized elements such as alkali and alkaline earth elements. The net result of ionization interferences is an increase or decrease in the intensity of emission lines for these elements. Few ionization interferences occur for these elements in ICP-AES.

Spectral interferences can be common in high temperature plasmas as opposed to flame-based systems given the complete excitation and subsequent emission of all compounds in the sample (including the argon). Spectral interferences can be divided into three different classes. The first type is spectral line coincidence when resolution of the monochromator of the system is too poor to separate the analyte line from a matrix line. The use of Echelle monochromators with higher resolution eliminates spectral interferences. The second cause of interferences occurs when a wavelength of interest overlaps completely with a nearby "broadened line wing". This can be solved by monitoring a secondary emission line for that particular element. Most

instruments use a background correction technique to overcome this type of interference. The final type of spectra interference referred to as spectral continuum occurs when stray light results from the recombination of electrons with Ar ions in the plasma that emits multiple intense lines. This can be avoided in some instruments by adjusting the temperature of the plasma or monitoring alternate lines. Stray light from matrix emissions can be avoided by use of high-end optical components such as “solar-blind PMTs”.

#### 4.5 Summary

Optical spectrometry has made considerable advances since the first flame-based instruments were introduced in the 1960s. Recent advances in plasma technology, monochromator layout, and computer-based detector systems such as charge transfer devices have given a new meaning to “state-of-the-art” technology. Today, low-end FAAS instruments are only used in situations where only one or two elements are analyzed infrequently. High sample throughput situations, such as those found in industry and environmental monitoring, require automated systems that can perform multiple analyses in a minimum amount of time. But these demands are paid for with instruments of significantly higher cost. While ICP-AES detection limits are significantly better than flame-based techniques, mass spectrometry yields even better detection limits and can distinguish between different isotopes. This is the subject of Chapter 5.

#### 3.6 Questions

Approximately how many elements can FAAS be used to analyze?

Approximately how many elements can ICP-AES or ICP-MS be used to analyze?

Why can ICP be used to analyze more elements than FAES?

Why is acid added to all samples during sampling or for sample digestion in FAAS, FAES, and ICP analysis?

Draw and explain how a Rowland circle of PMTs is used in ICP-AES.

Explain the purpose and operation of the nebulizer in the ICP.

What is the most common type of nebulizer in ICP?

List all of the types of sample introduction to plasma.

What is a plasma?

What is ohmic heating?

Write a detailed discussion explaining how an ICP plasma is “light” and maintained.

Explain the name “inductively coupled plasma.”

Why does the plasma not melt the instrument? How is it cooled?

Explain the three zones present in the plasma.

Contrast the separation of wavelengths by the two different systems in Figures 4.7 and 4.8.

List and explain the types of interferences in ICP-AES.