

In the Classroom

Inductively Coupled Plasma - Atomic Emission Spectrometry

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*The basic aim
of analytical
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Analytical chemistry is the science of accurate and precise qualitative and quantitative measurements involving chemical systems. Spectroscopy is defined as the interaction of light and matter and has both physical and analytical applications. Physical spectroscopists use emitted light, absorbed light, or scattered light in order to understand the mechanics of a chemical system. Analytical spectroscopists use the same physical processes to determine the content and concentration of the atomic and molecular species present in a chemical system.

In the past 20 years the number of instrumental techniques available to the chemist has grown exponentially. In order to help our readers keep up with this rapidly growing field, tutorial articles on chemical instrumentation will be a regular feature of *The Chemical Educator*. The articles are designed to serve as a brief introduction to emerging instrumental techniques with an outline of the underlying principles and major applications.

—Martin Schimpf, Series Editor

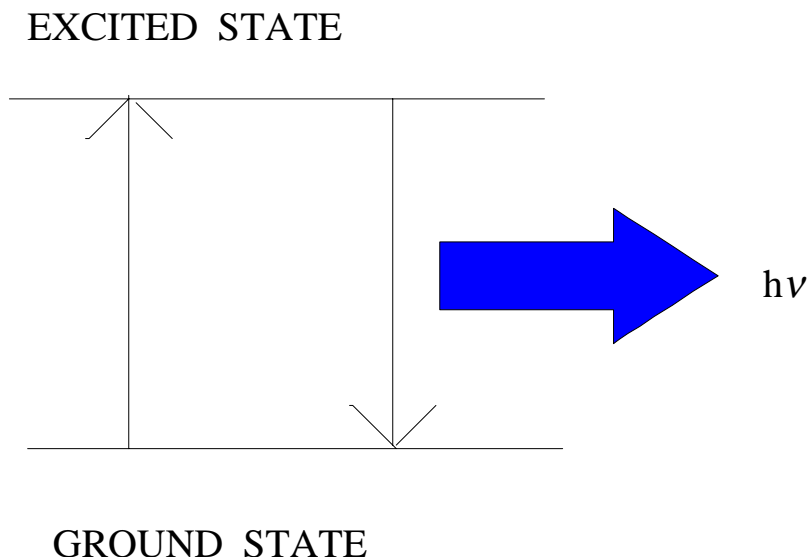


FIGURE 1. EMISSION OF RADIATION UPON RELAXATION FROM AN EXCITED STATE.

As illustrated in Figure 1, atoms emit electromagnetic radiation ($h\nu$) as they relax from an excited state to their ground state. The emitted radiation can be easily detected when it is in the vacuum ultraviolet (VUV, 120–185 nm), ultraviolet (UV, 185–400 nm), visible (VIS, 400–700 nm), and near infrared regions (NIR, 700–850 nm). Although atoms emit electromagnetic radiation in the infrared, microwave, and radiowave regions, the detection systems are less sensitive in these regions; therefore, the VUV, UV, VIS, and NIR regions are preferred. Of these only the VUV needs a special environment devoid of air. Nevertheless, a portion of the VUV spectrum is used by analytical spectroscopists.

The basic aim of analytical atomic spectroscopy is to identify elements and quantify their concentrations in various media. The procedure consists of three general steps: atom formation, excitation, and emission. Before excitation, an element that is bound in a specific matrix must be separated from that matrix so that its atomic emission spectra is free from interferences. For UV and visible spectroscopy, the input energy must be sufficient to raise an electron from the ground state to the excited state. Once the electron is in the excited state, the atom emits light, which is characteristic of that particular element. This tutorial will compare the Inductively Coupled Plasma (ICP)

excitation source to other techniques while covering methods of sample introduction, detection, and fundamental plasma processes.

The perfect atomic emission source would have the following characteristics:

1. Complete removal of the sample from its original matrix in order to minimize interferences.
2. Complete atomization but minimum ionization of all elements to be analyzed.
3. A controllable energy source for excitation, which allows the proper energy needed to excite all elements without appreciable ionization.
4. An inert chemical environment, which prohibits the formation of undesirable molecular species (e.g. oxides, carbides, etc.) that affect the accuracy of the measurement.
5. No background radiation from the source. Background radiation is defined as unwanted atomic or molecular emission that could interfere with the analytical wavelengths.
6. A source that can handle a range of solvents, both organic and inorganic in nature.
7. A source that is adjustable to handle solids, slurries, liquids, or gases.
8. Inexpensive to purchase and maintain.
9. Easy to operate.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is one of several techniques available in analytical atomic spectroscopy. ICP-AES utilizes a plasma as the atomization and excitation source. A plasma is an electrically neutral, highly ionized gas that consists of ions, electrons, and atoms. The sun, lightning, and the aurora borealis are examples of plasmas found in nature. The energy that maintains an analytical plasma is derived from an electric or magnetic field; they do not “burn.” Most analytical plasmas operate with pure argon or helium, which makes combustion

1. Sample Preparation: Some samples require special preparation steps including treatment with acids, heating, and microwave digestion.

2. Nebulization: Liquid converted to aerosol.

3. Desolvation/Volatization: Water is driven off, and remaining solid and liquid portions are converted to gases.

4. Atomization: Gas phase bonds are broken, and only atoms are present. Plasma temperature and inert chemical environment are important at this stage.

5. Excitation/Emission: Atoms gain energy from collisions and emit light of a characteristic Wavelength.

6. Separation/Detection: A grating disperses light that is quantitatively measured.

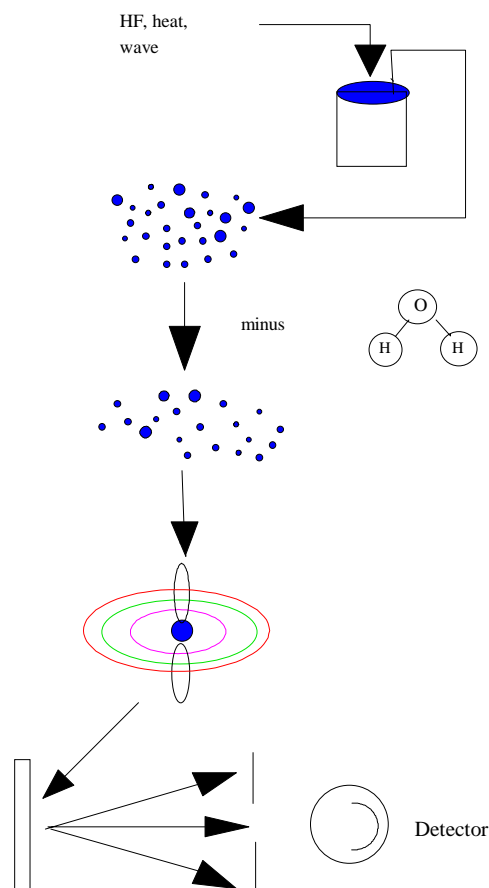


FIGURE 2. STEPS INVOLVED IN THE ANALYSIS OF AQUEOUS SAMPLES BY ICP-AES.

impossible. Plasmas are characterized by their temperature, as well as their electron and ion densities. Analytical plasmas typically range in temperature from 600 to 8,000 K. As a comparison, the temperature of the sun's interior is millions of degrees, while its surface temperature is approximately 10,000 K. Figure 2 summarizes the steps involved in determining the elemental content of an aqueous phase sample by ICP-AES.

Comparison Of Techniques

Table 1 compares several features of common techniques used for atomic spectroscopy. The techniques can be considered as belonging to one of three categories: flames, furnaces (electrothermal), and plasmas. Each technique has advantages and disadvantages in performance, versatility, and price. It should be noted

TABLE 1. Summary of common techniques used atomic spectroscopy.

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

¹ Inductively Coupled Plasma-Atomic Emission Spectrometer.

² Flame Atomic Absorption.

³ Graphite Furnace Atomic Absorption.

⁴ Microwave Induced Plasma.

⁵ DC plasma arc.

⁶ The limit of detection for iron by concentration (MIP-AES is used primarily for nonmetals).

⁷ The limit of detection for iron by absolute mass (for ICP, FAA, DCP assumes 2 mL volume, GFAA assumes 50 μL).

⁸ Single or multielement analysis possible on a single sample. For example, a commercial ICP can simultaneously detect 20 elements but a graphite furnace atomic absorption system is only capable of single element detection with a single "shot."

⁹ The linear dynamic range (orders of magnitude).

¹⁰ The wavelength range of the technique. These values can vary with sources, dispersing element, and detector chosen.

¹¹ Varies with vendor, model, accessories, etc..

¹² Interferences from instrumental system.

¹³ Ar emission; continuum background.

¹⁴ Molecular emission; absorbance from gas species (e.g., C₂, N₂, CO, etc.).

¹⁵ Scattering from particulate matter.

¹⁶ Helium emission.

¹⁷ Electrode degradation (e.g., W, WC, emission etc.).

that most parameters will vary with model, year, operator, operating conditions, matrix, etc.. Values given for most parameters should be considered as typical.

The ICP Torch

The ICP is a radiofrequency-(RF, 27.12 MHz, 40 MHz) induced plasma that uses an induction coil to produce a magnetic field (H). The ICP operates between 1 and 5 kilowatts. The induction coil is wrapped two or three times around the ICP torch and has water flowing through it for cooling purposes. All ICPs have a capacitor bank that is continuously tuned to match the plasma's inductance. In order for the RF to travel along the surface of the hollow coil with minimum resistance, the coil is either gold or silver plated. Neither gold or silver forms metal oxides upon contact with air. Although the RF power supply maintains the plasma, a tesla coil is used to ignite the plasma through the generation electrons and ions that couple with the magnetic field.

The most common ICP torch in use today has evolved over decades of development (see Figure 3). The circular quartz tube (12–30 mm OD) has three separate gas inlets. The only gas routinely used is argon. The gas enters the plasma through the outer channel with a tangential flow pattern at a rate of 8–20 Lmin⁻¹. The auxiliary gas, which travels up the center channel, also has a tangential flow (0.5–3 L min⁻¹) pattern. The nebulizer gas has a laminar flow pattern (0.1 to 1.0 Lmin⁻¹) and injects the sample into the plasma. The analytical zone is approximately 1 cm above the coils and offers the best optical viewing area for maximum sensitivity.

The plasma temperature in the analytical zone ranges from 5000–8000 K (the temperature varies with power, flow rate, etc.). The high temperature assures that most samples are completely atomized, although some molecular species (e.g., N₂, N₂⁺, OH, C₂, etc.) do exist and can be readily measured in the plasma.

The plasma emits a continuum of background radiation that extends from the visible into the ultraviolet region (see Figure 4). The radiation originates from electrons, Ar and Ar⁺, as well as various atomic and molecular species in the matrix. Although sample blanks can help offset the unwanted flux of background photons, there is a certain level of instability in the continuum background and this instability plays a role in limiting the sensitivity of ICP-AES.

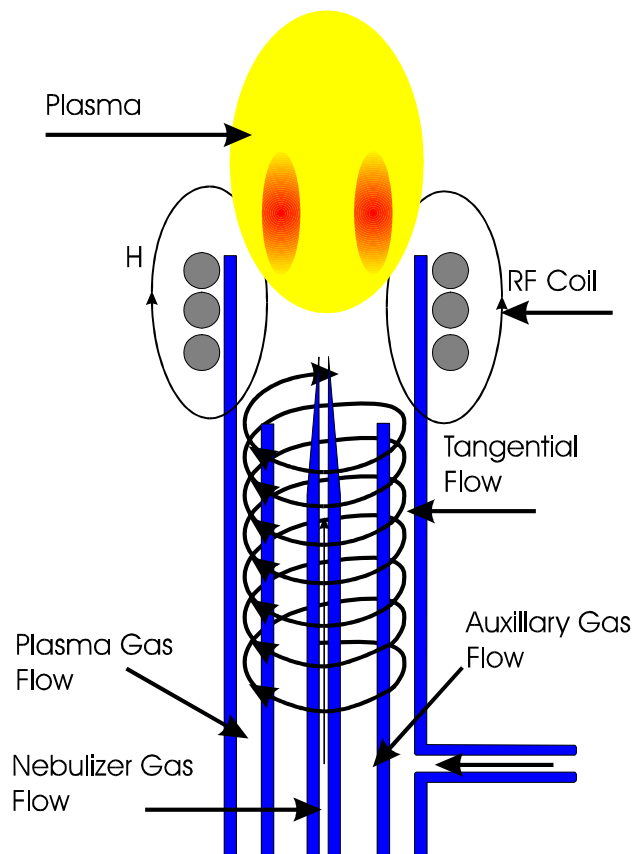


FIGURE 3. SCHEMATIC OF AN ICP TORCH.

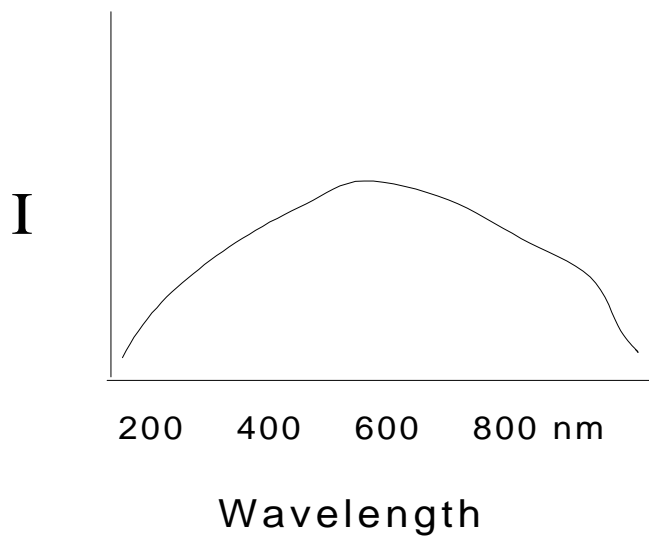


FIGURE 4. THE INTENSITY (I) OF AN ARGON PLASMA VERSUS WAVELENGTH OF EMISSION.

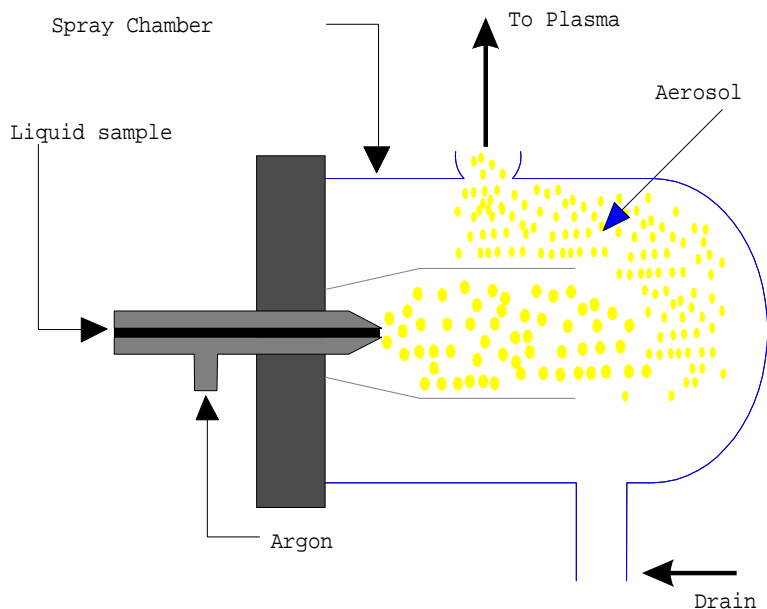


FIGURE 5. A PNEUMATIC NEBULIZER THAT USES THE BERNOULLI EFFECT FOR SAMPLE UPTAKE.

Sample Introduction

All three states (solid, liquid, gas) have been successfully introduced into an ICP. Although both aqueous and nonaqueous solvents have been utilized, the most commonly analyzed sample is cations in solution. For solutions, a nebulizer is used to convert the liquid stream into an aerosol consisting of particles that are 1–10 μm in diameter. Direct injection of liquids into the plasma would either extinguish the plasma or cause the atoms to be improperly desolvated, making excitation and emission less efficient. Five common sample introduction devices for solution samples are discussed below.

Pneumatic Nebulizer

Figures 5 and 6 illustrate two pneumatic nebulizers, which are the most common type of nebulizer in use today. In Figure 5 the sample solution is drawn through a capillary by the flow of a nebulizing gas (the so-called Bernoulli effect). The aerosol generated in the spray chamber is separated by size with smaller drops being carried to the plasma; the larger drops are drained. In Figure 6, the sample and nebulizing gases

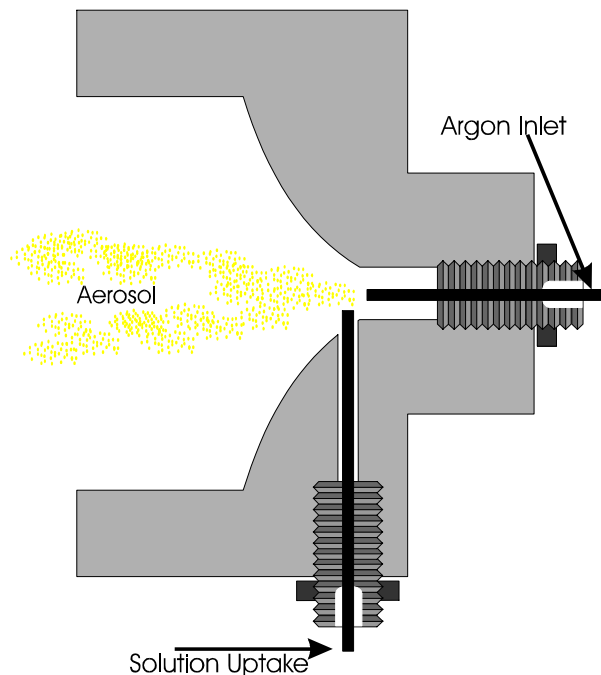


FIGURE 6. A PNEUMATIC NEBULIZER IN WHICH THE SAMPLE AND NEBULIZING GAS COMBINE AT RIGHT ANGLES TO FORM AN AEROSOL.

combine at a right angle, causing the sample to form an aerosol, which subsequently strikes an impact bead (not shown). The impact bead causes the drops to break apart.

Frit Nebulizer

Figure 7 illustrates a glass-frit nebulizer. The sample solution is pumped to the frit membrane, which consists of a porous man-made material similar in texture to coral. Argon passes through the membrane and causes the sample to form an aerosol spray. Frit nebulizers have efficiencies as high as 90% with excess sample being drained. The system is equipped with a wash solution inlet to clean the frit membrane and avoid memory effects.

Ultrasonic Nebulizer

Figure 8 illustrates an ultrasonic nebulizer. In this device, a piezoelectric crystal vibrates at ultrasonic frequencies (50 kHz to 4 MHz), and the sample is pumped to the crystal through a small plastic tube. The vibrations of the crystals cause the droplets to break up into smaller particles, which are transported to the plasma. Larger aerosol drops are drained.

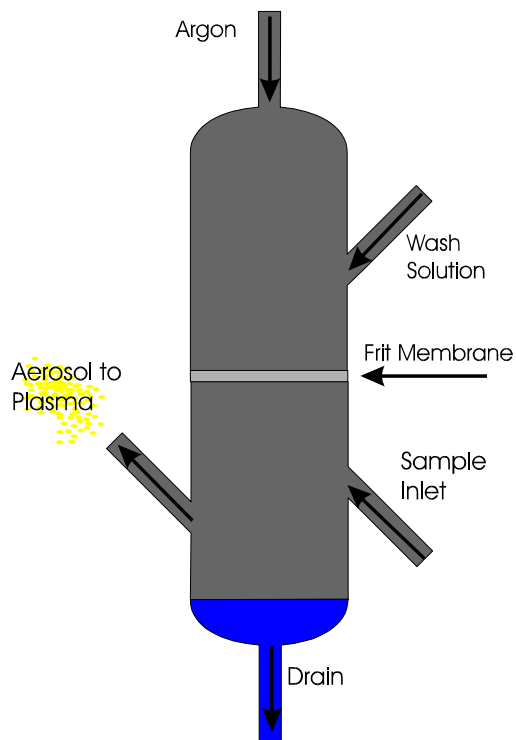


FIGURE 7. FRIT NEBULIZER.

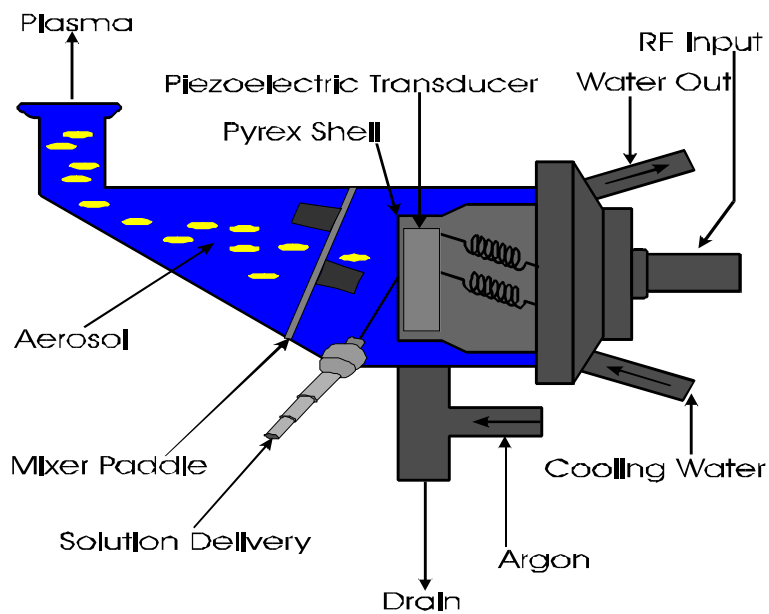


FIGURE 8. ULTRASONIC NEBULIZER.

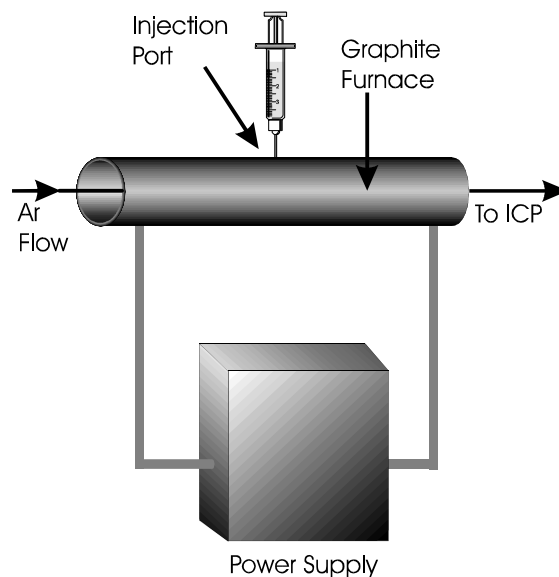


FIGURE 9. ELECTROTHERMAL VAPORIZER.

Electrothermal Vaporizer

Electrothermal vaporization, which is illustrated in Figure 9, has been used for both solid and liquid samples. For liquids a finite quantity (5–50 μl) is placed in a graphite furnace, which is subsequently heated electrically. The resulting vaporized sample is sent to the plasma for analysis. The temperature in the sample is ramped from a relatively low temperature (e.g., 110 $^{\circ}\text{C}$), which drives off the solvent, to a higher temperature (e.g., 2000 $^{\circ}\text{C}$), which causes the remaining solid to vaporize.

Hydride Generator

Metalloids and soft metals (e.g., As, Se, Sb, Sn) can be introduced into the ICP in the form of a volatile hydride, which is formed by reacting the element of interest with sodium borohydride (NaBH_4). The gaseous hydride is then carried to the plasma for analysis.

The analysis of solids by ICP-AES is a rapidly expanding field. Samples that can be analyzed range from viscous slurries to pieces of alloys. Solids are introduced into the plasma either directly or after electrothermal vaporization, arc vaporization, or laser ablation. For direct insertion, a probe with a finite amount of sample on its tip is used to introduce the sample into the plasma. In a DC arc, which is illustrated in Figure 10, a small amount of solid sample is mounted on an electrode and vaporized by the an electric current before being transported to the ICP. Direct laser ablation, which is

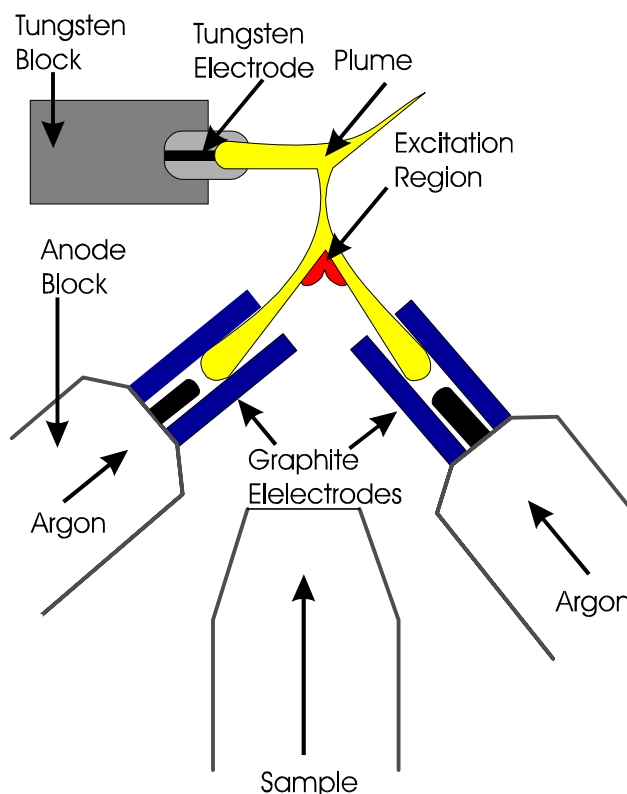


FIGURE 10. DC ARC SAMPLE INTRODUCTION DEVICE.

illustrated in Figure 11, utilizes a pulsed laser to vaporize the solid sample. The plume is carried by argon gas to the ICP torch for analysis by AES. The laser plume is generated in an inert environment minimize combustion or metal oxide formation.

Dispersion and Detection Methods

There are three common devices used for the separation or dispersion of light: gratings, prisms, and Michelson interferometers. There are four basic types of detector systems: photomultiplier tubes (PMTs), photo diode arrays (PDAs), and charge coupled devices (CCDs). These dispersion and detection devices are typically combined in one of four configurations, which vary in sophistication: (1) Sequential; (2) simultaneous with single-point detection; (3) simultaneous with one-dimensional detection; and (4) simultaneous with two-dimensional detection.

Sequential systems utilize a prism or grating and a PMT. This configuration, which is illustrated in Figure 12, is often referred to as a monochromator. Sequential systems

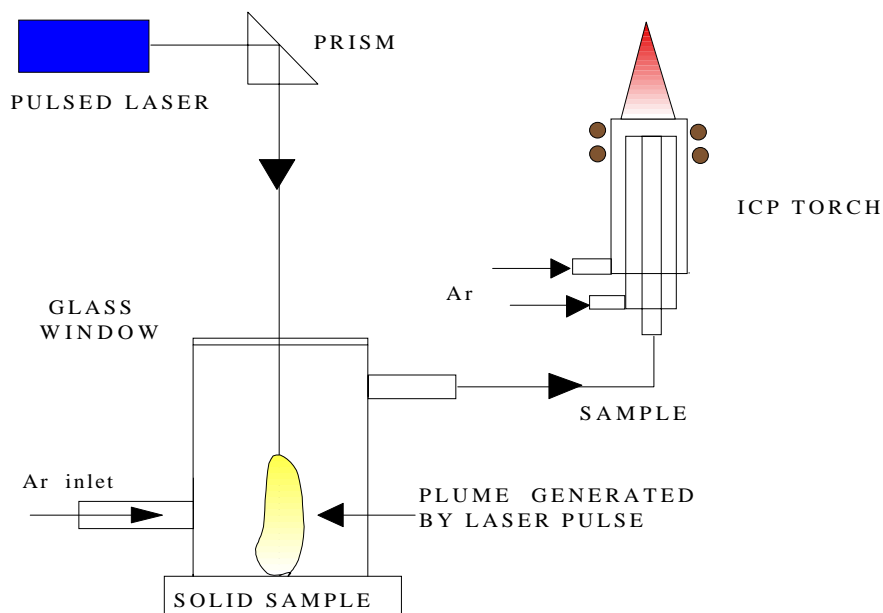


FIGURE 11. SAMPLE INTRODUCTION BY LASER ABLATION.

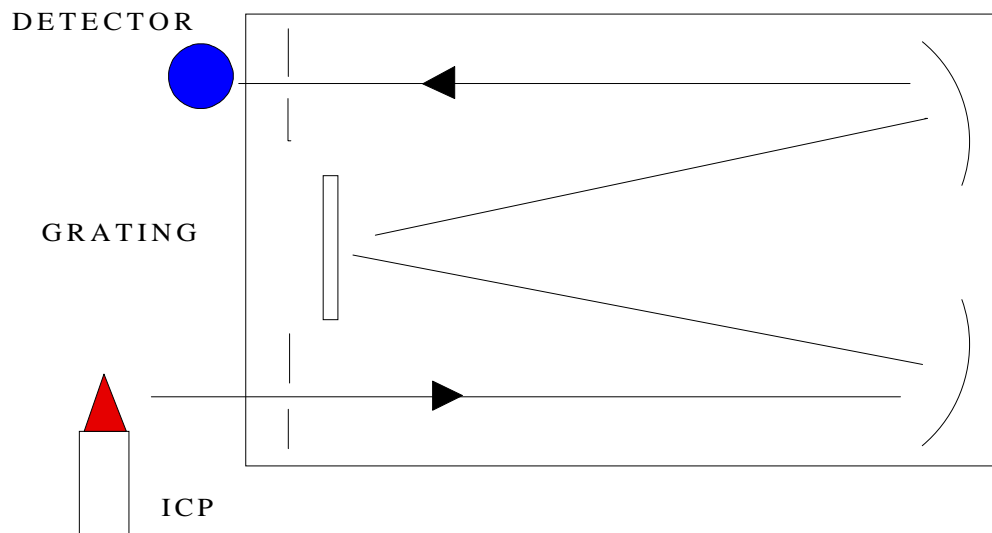


FIGURE 12. A MONOCHROMATOR FOR SEQUENTIAL ANALYSIS OF RADIATION.

allow for the analysis of only one analytical line at a time, which is time consuming. To scan an entire region of the electromagnetic spectrum with a sequential system, the detector is held at a fixed position and the grating is turned sequentially.

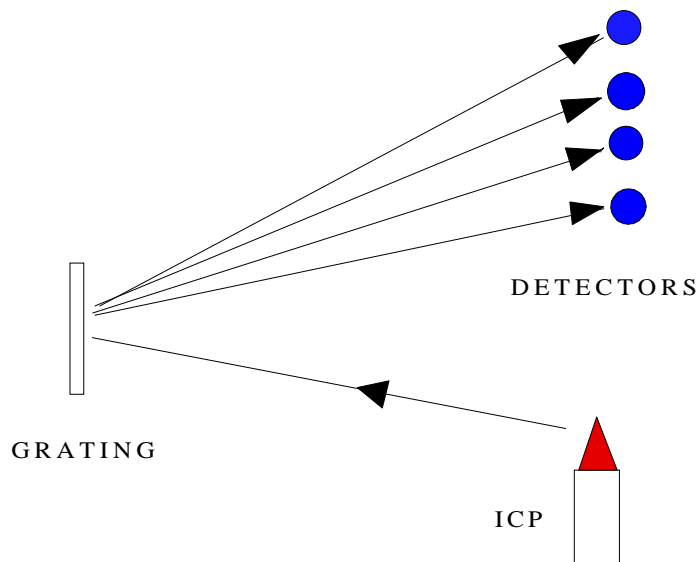


FIGURE 13. A POLYCHROMATOR FOR SIMULTANEOUS ANALYSIS OF RADIATION.

More efficient systems measure specific wavelengths at multiple positions simultaneously, as illustrated in Figure 13. The ability of these so-called polychromators to measure more than one analytical line at a time, is a distinct advantage over monochromators, but polychromators suffer from a lack of flexibility. Thus, once the dispersion and detection systems are set, only certain analytical lines and elements may be measured.

The next generation involves the use of a one-dimensional solid state detector called a photodiode array. The PDA, which is illustrated in Figure 14, is similar to a PMT in that the detectors are in a fixed position, but the PDA detectors are smaller and less expensive. As a result, more detectors can be incorporated into a single instrument. A typical PDA will hold 1,024 miniature detectors that measure energy simultaneously in a two- to three-inch space. This allows for spectral windows in the 50–100 nm range to be simultaneously measured.

A charge coupled device is an extension of solid state detector technology into two dimensions (e.g., 300 by 500 pixels). Combining a prism and grating with a CCD (see Figure 15) allows for multielement analysis using more than 1 wavelength per element. Each pixel discharges a current proportional to the energy striking it. CCDs commonly use a grating in conjunction with a prism to disperse the spectral radiance as a function of energy and order in two dimensions.

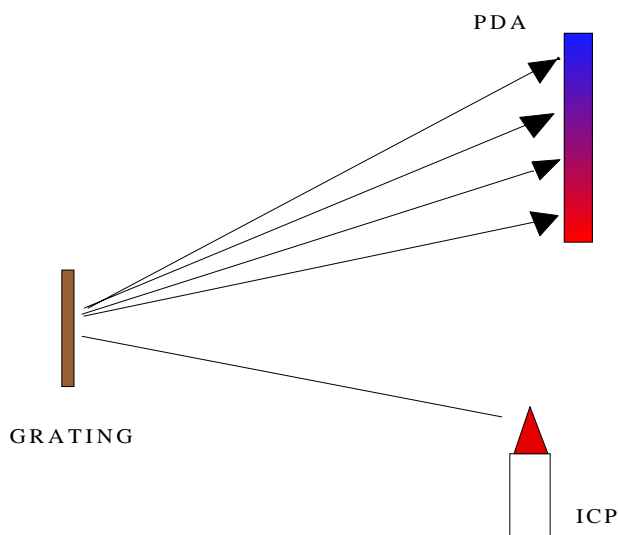


FIGURE 14. A PHOTODIODE ARRAY FOR SIMULTANEOUS ANALYSIS OF RADIATION.

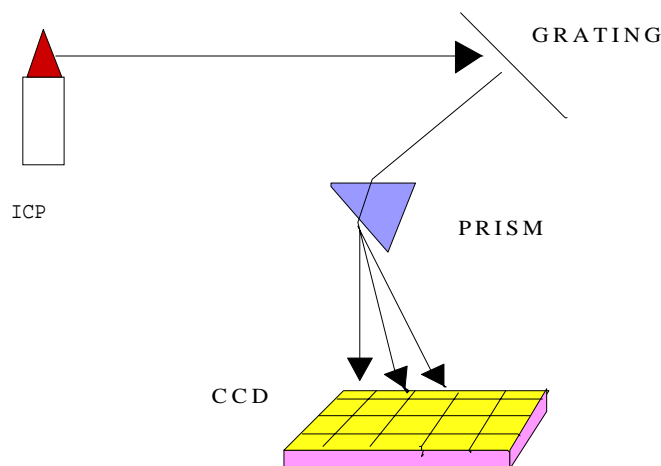


FIGURE 15. TWO-DIMENSIONAL DISPERSION AND DETECTION OF RADIATION USING A CHARGE-COUPLED DEVICE (CCD).

Interferences

Any chemical or physical process that adversely affects the measurement of the radiation of interest can be classified as an interference. Interferences in ICP-AES may start in the sample preparation stage and extend to the plasma operating conditions.

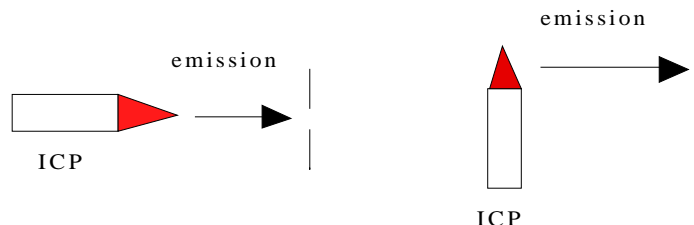


FIGURE 16. ICP TORCH POSITIONS INCLUDE A HORIZONTAL MOUNT (LEFT) AND THE MORE TRADITIONAL VERTICAL MOUNT (RIGHT).

The first type of common interference involves two or more elements in the matrix emitting radiation at the same wavelength (e.g., Cu at 515.323 nm and Ar at 515.139 nm). These spectral interferences can be minimized by using a high resolution system by using several analytical lines for the detection of a single element. A second type of interference involves the formation of undesired species (e.g., ions, metal oxides). For example, some metals are extremely sensitive to small plasma fluctuations in terms of their relative neutral atom and ion densities. It is important to note that an atom of a specific element (e.g., Fe) has a different emission spectra than one of its ions (e.g., Fe^+ , Fe^{+2} , etc.). Other interferences, such as the formation of metal oxides or metal carbides, have to be evaluated on an individual basis.

Sensitivity

Table 2 lists typical limits of detection obtained with a commercial ICP-AES for over 70 elements. The units are in parts per billion (e.g., ng mL^{-1} or $\mu\text{g L}^{-1}$). Inert gases and some prominent nonmetals (C, N, O, H) are not analyzed by ICP-AES. There are two ICP torch positions that can be purchased; these are illustrated in Figure 16. The horizontal position is relatively new and offers better LODs than the traditional mount.

Trends

Inductively Coupled Plasma -Atomic Emission Spectroscopy is an analytical technique that has reached maturity in many respects. There are several collected works and textbooks available at this time [1, 2]. Since its introduction [3–5], the ICP has evolved not only as an atom and ion reservoir for emission spectroscopy, but as an ion source

TABLE 2. Elements and their limit of detection by ICP-AES.

Element	LOD	Element	LOD	Element	LOD
Ag	0.9	Hg	1	Sb	10
Al	3	Ho	0.4	Sc	0.2
As	50	I		Se	50
Au	8	In	9	Si	3
B	0.8	Ir	5	Sm	2
Ba	0.09	K	20	Sn	60
Be	0.08	La	1	Sr	0.03
Bi	30	Li	0.3	Ta	10
Br		Lu	0.2	Tb	2
C	75	Mg	0.07	Te	10
Ca	0.02	Mn	0.4	Th	
Cd	1	Mo	3	Ti	0.4
Ce	5	Na	3	Tl	30
Cl		Nb	10	Tm	0.6
Co	1	Nd	2	U	15
Cr	2	Ni	5	V	0.5
Cs		Os	6	W	8
Cu	0.4	P	30	Y	0.3
Dy	2	Pb	10	Yb	0.3
Er	1	Pd	3	Zn	1
Eu	0.2	Pr	2	Zr	0.7
F		Pt	10		
Fe	2	Rb	30	He, Ne	
Ga	4	Re	5	Ar	
Gd	0.9	Rh	5	Kr, Xe	
Ge	20	Ru	6	H, O	
Hf	4	S	30	N, C	

for mass spectrometry (ICP-MS) [6]. Although ICP-MS is more expensive than ICP-AES, it offers substantial improvements in sensitivity and has the ability to identify isotopes. The majority of papers being published at this time concerning ICP-AES deal with new-methods development and sample preparation.

Common Questions About ICP-AES

1. Why not use air or nitrogen as the carrier gas in an ICP?

Isn't argon expensive? Argon is 0.9% of the earth's atmosphere, so it is readily available. N_2 emits several molecular bands in the ultraviolet and visible so overlaps with analytical lines are possible. Despite this limitation, there have been successful applications of nitrogen as the carrier gas in ICP-AES.

2. What is the major drawback to elemental analysis by ICP-AES?

One major drawback to ICP-AES is that it does not identify the oxidation state of the element in its original matrix. For example, a sample may contain Fe^{+3} but when the iron is detected in the plasma, it will be predominantly Fe with some Fe^+ .

3. Can the ICP detect nonmetals?

Yes! Many of the nonmetals (e.g., P, S, halogens) have strong emission lines that are in the vacuum ultraviolet. As more instruments come equipped with VUV capabilities, analysis of nonmetals by ICP-AES will expand.

4. What is the system for identifying oxidation numbers in the gas phase?

Spectroscopists and chemists identify elemental oxidation numbers differently. In spectroscopy, neutral or atomic copper is Cu I, and singly-charged copper is Cu II. In solution chemistry, atomic copper is Cu, while singly-charged copper is Cu I (Cu^+) and doubly-charged copper would be Cu II (Cu^{+2}).

5. Why is there no Fourier Transform-UV/VIS ICP spectrometers?

This does exist, but only as a research tool. Its advantages include high resolution, high wavelength accuracy, throughput advantage, intensity precision

and accuracy, and the multiplex advantage (simultaneous acquisition of all wavelengths). Disadvantages include the noise generated by simultaneous acquisition of all wavelengths (multiplex disadvantage) and optical flatness and mirror movement accuracy and precision constraints that are much more stringent and difficult to achieve with the shorter wavelength UV/VIS region than the relatively long wavelength IR radiation.

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