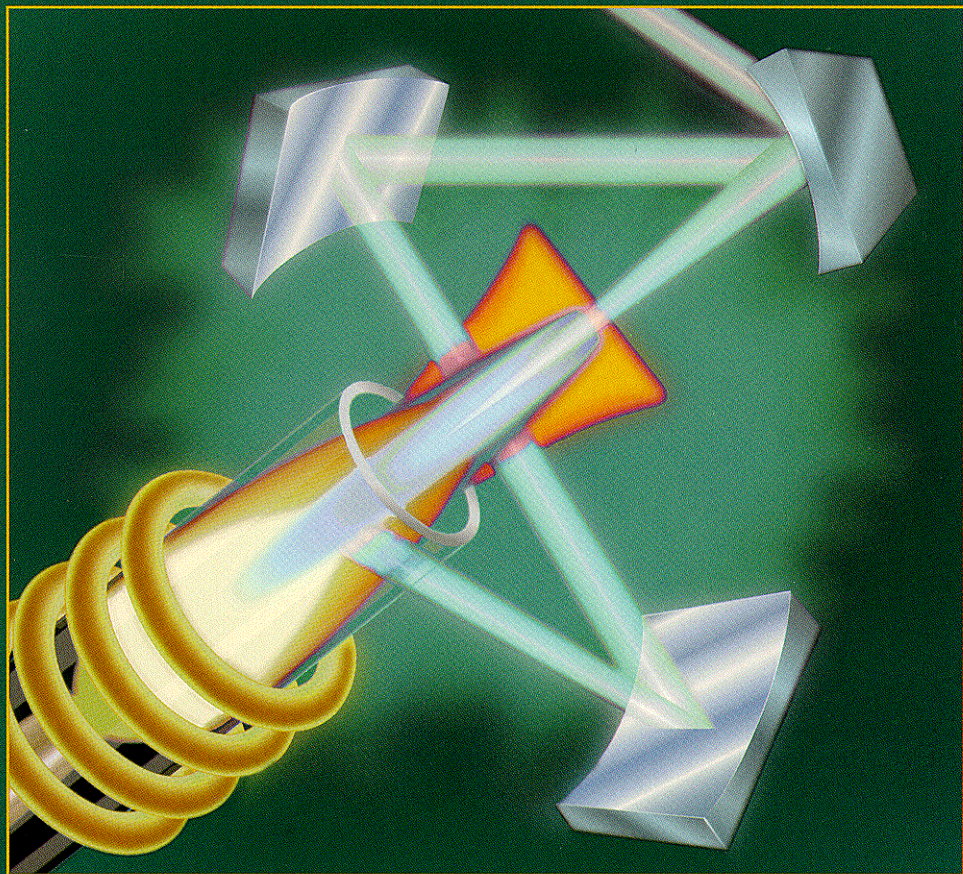


Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry

Charles B. Boss and Kenneth J. Fredeen



PERKIN ELMER

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Second Edition

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PREFACE

The widely used analytical technique for the determination of trace elements, inductively coupled plasma–optical emission spectrometry (ICP–OES), marked its thirty-third anniversary in 1997. [In this book, the technique will be referred to as ICP–OES though the reader may notice that many technical publications refer to it as inductively coupled plasma–atomic emission spectrometry (ICP–AES). Unfortunately, the latter designation is sometimes confused with Auger Electron Spectrometry (AES). In the interest of clarity, therefore, the term "inductively coupled plasma - optical emission spectrometry" (ICP–OES) has been rigidly adopted.]

Many advances have been made since the first commercial ICP-OES instruments were introduced to the analytical community. Advancements in the understanding of the ICP source and the measurement of emission signals have led to many improvements in the design of the components that comprise the instruments used for ICP-OES. Other advances have resulted through the use of computers with these instruments and the increasing levels of automation and sophistication that they help to realize.

Despite the advances in ICP-OES instrumentation and software, ICP-OES is not a "foolproof" technique. Because ICP-OES is a sensitive trace analysis technique, care must be taken in the preparation of standards, blanks and samples introduced into the instrument. The instrumentation must be set up properly and parameters, such as wavelengths and background correction points, must be selected to fit the application. Attention to details seemingly as minor as changing the peristaltic pump tubing when it is worn can make the difference between acceptable and unacceptable analysis results.

There are several sources of specific, detailed information about the ICP-OES technique available. It was felt, however, that there was still a need for a general introductory guide for new and potential users of ICP-OES. Such a guide should provide basic, practical information to help new users better understand the fundamentals behind, and requirements for, performing good analyses using the ICP-OES technique.

This book is intended as that introduction to the ICP-OES technique. It was written not only for those persons who have some familiarity with other analytical techniques such as atomic absorption spectrometry but also for novices in the field of analytical chemistry. The book begins with some simple, yet fundamental, concepts regarding atomic spectroscopy and the analytical techniques based on this field of study. As one progresses through the book, more detail regarding the ICP-OES technique is

presented including information about ICP-OES performance, instrumentation and methodology.

The final chapter of the book briefly describes some representative ICP-OES applications. The reader should not be alarmed if his or her particular application is not mentioned here. So many different ICP-OES applications have been developed in the last thirty-three years that it would be difficult to describe them all in a single volume. We have also included in an appendix some information about instrument maintenance and performance verification. While this kind of practical information can be vital to obtaining good analytical results, it is sometimes difficult to find.

Finally, in the back of this book there is a glossary of terms as they are commonly used in atomic spectroscopy. The reader may find it helpful to refer occasionally to this section for further details regarding terms that are used in the main body of the book.

We hope that this introduction to the ICP-OES technique will provide useful information to those persons who are about to get involved with ICP-OES as well as present ICP users and those with simply a curiosity about the technique.

1 AN OVERVIEW OF ELEMENTAL ANALYSIS VIA ATOMIC SPECTROSCOPY TECHNIQUES

One of the simplest questions that an analyst can ask about the chemical composition of a sample is "which elements are present and at what concentrations?" Since there are only 92 naturally occurring elements and millions of different molecules, differentiating among the elements is a much easier task than differentiating among the molecules. Nonetheless, the elemental composition of a sample is often an important part of the information needed to assess its properties.

For example, consider a water sample which is determined to contain 88.2% oxygen and 11.0% hydrogen by mass, meaning that only 99.2% of the sample could be made up of water molecules. Whether the water from which this sample was taken is useful for a particular purpose may well depend on the remaining 0.8%. If this water sample contained as much as a microgram of boron per gram of sample (0.0001% of the mass), the water would be perfectly useful for most purposes. If, however, you wanted to use that water in the fabrication of ceramic turbine blades for jet engines, purification would be required. When water containing as much as one part per million boron is used in the manufacture of the ceramics for these turbine blades, their failure rate rises dramatically. Research has shown that boron collects on the grain boundaries of the ceramic turbine blades, causing fractures that have been implicated in catastrophic failures of jet engines.

There are many other examples of the need for determining the trace level concentrations of elements within samples. For example, the United States Environmental Protection Agency has strict rules concerning trace levels of dangerous metals allowed in wastewaters. Some of these limits are in the parts per billion range. Determination of elemental concentrations at these trace levels requires the use of sensitive scientific instrumentation.

The most commonly used techniques for the determination of trace concentrations of elements in sample are based on atomic spectrometry. As the name atomic spectrometry implies, these techniques involve electromagnetic radiation (light) that is absorbed by and/or emitted from atoms of a sample. (Not implicit in the term

"atomic spectrometry", however, is that we generally include emission and absorption of electromagnetic radiation by charged atoms, or *ions*, also under the heading of atomic spectrometry.) By using atomic spectrometry techniques, meaningful quantitative and qualitative information about a sample can be obtained. In general, quantitative information (concentration) is related to the amount of electromagnetic radiation that is emitted or absorbed while qualitative information (what elements are present) is related to the wavelengths at which the radiation is absorbed or emitted.

An affiliated technique to atomic emission or absorption spectrometry is *atomic mass spectrometry*. In mass spectrometry, instead of obtaining analytical information from the radiation of atoms or ions, ions introduced into a mass spectrometer are separated according to their mass to charge ratio and are either qualitatively or quantitatively detected.

Nature of Atomic or Ionic Spectra

The measurement of absorption and emission of electromagnetic radiation can be more easily described once the nature of atomic and ionic spectra is understood. Consider the Bohr model of an atom shown in Figure 1-1. The atom is depicted as a nucleus surrounded by electrons which travel around the nucleus in discrete orbitals. Every atom has a number of orbitals in which it is possible for electrons to travel. Each of these electron orbitals has an energy level associated with it. In general, the further away from the nucleus an orbital, the higher its energy level.

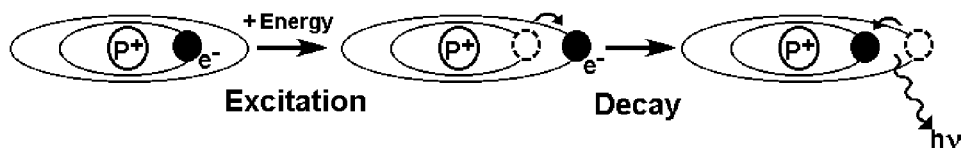


Figure 1-1. Bohr model of an atom. As energy is absorbed by an atom, an electron jumps to an orbital with a higher energy level. The atom may decay to a lower energy state by emitting a photon, $h\nu$.

When the electrons of an atom are in the orbitals closest to the nucleus and lowest in energy, the atom is in its most preferred and stable state, known as its *ground state*. When energy is added to the atom as the result of absorption of electromagnetic radiation or a collision with another particle (electron, atom, ion, or molecule), one or more of several possible phenomena take place. The two most probable events are for the energy to be used to increase the kinetic energy of the atom (*i.e.*, increase the velocity of the atom) or for the atom to absorb the energy and become excited. This latter process is known as *excitation*.

When an atom becomes excited, an electron from that atom is promoted from its ground state orbital into an orbital further from the nucleus and with a higher energy level. Such an atom is said to be in an *excited state*. An atom is less stable in its excited state and will thus decay back to a less excited state by losing energy through a collision with another particle or by emission of a "particle" of electromagnetic radiation, known as a *photon*. As a result of this energy loss, the electron returns to an orbital closer to the nucleus.

If the energy absorbed by an atom is high enough, an electron may be completely dissociated from the atom, leaving an ion with a net positive charge. The energy required for this process, known as ionization, is called the ionization potential and is different for each element. Ions also have ground and excited states through which they can absorb and emit energy by the same excitation and decay processes as an atom.

Figure 1-2 shows the excitation, ionization and emission processes schematically. The horizontal lines of this simplified diagram represent the energy levels of an atom. The vertical arrows represent *energy transitions*, or changes in the amount of energy of an electron. The energy transitions in an atom or ion can be either *radiational* (involving absorption or emission of electromagnetic radiation) or *thermal* (involving energy transfer through collisions with other particles).

The difference in energy between the upper and lower energy levels of a radiative transition defines the wavelength of the radiation that is involved in that transition.

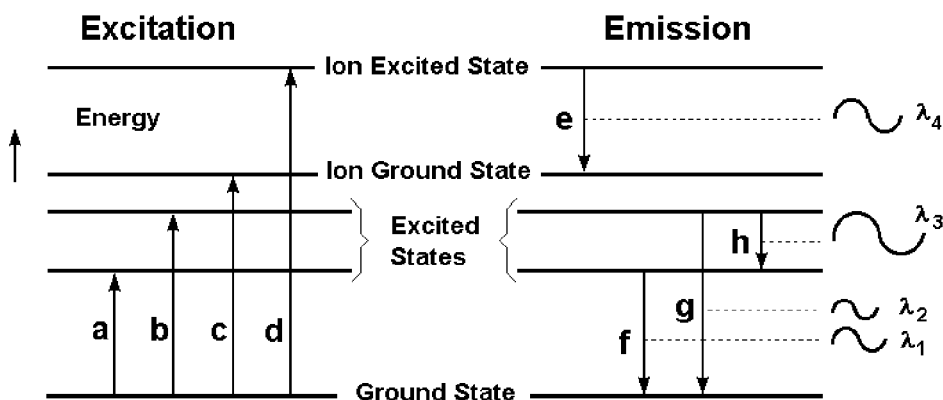


Figure 1-2. Energy level diagram depicting energy transitions where **a** and **b** represent excitation, **c** is ionization, **d** is ionization/excitation, **e** is ion emission, and **f**, **g** and **h** are atom emission.

The relationship between this energy difference and wavelength can be derived through Planck's equation

$$E = h\nu$$

where **E** is the energy difference between two levels, **h** is Planck's constant, and ν is the frequency of the radiation. Substituting c/λ for ν , where **c** is the speed of light and λ is wavelength, we get

$$E = hc/\lambda$$

This equation shows that energy and wavelength are inversely related, *i.e.*, as the energy increases, the wavelength decreases, and *vice versa*. Using Figure 1-2 as an example, the wavelength for emission transition **f** is longer than the wavelength for emission transition **g** since the energy difference for **f** is less than for transition **g**.

Every element has its own characteristic set of energy levels and thus its own unique set of absorption and emission wavelengths. It is this property that makes atomic spectrometry useful for element-specific analytical techniques.

The ultraviolet(UV)/visible region (160 - 800 nm) of the electromagnetic spectrum is the region most commonly used for analytical atomic spectrometry. This is also the region of the electromagnetic spectrum that we generally refer to as "light", although technically, all electromagnetic radiation can be considered as light. For further discussions in this book, the term "light" will often be used in place of "UV/visible electromagnetic radiation".

The principal reasons for the popularity of analytical techniques that use the UV/visible region are that these techniques are accurate, precise, flexible, and relatively inexpensive compared to techniques which use other regions, such as gamma ray spectrometry and X-ray spectrometry. Many of the devices used in UV/visible atomic spectrometry, such as photomultipliers and gratings, are relatively inexpensive since they were developed for and are commonly used in high-volume applications. Also, unlike gamma rays and X-rays, UV/visible radiation is not ionizing radiation. This lessens the expenses associated with shielding and licensing of the laboratory and with disposal of analyzed samples.

Analytical Techniques Based on Atomic Spectrometry

In the atomic spectrometry techniques most commonly used for trace element analysis, the sample is decomposed by intense heat into a cloud of hot gases

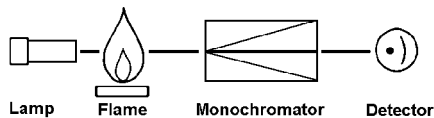
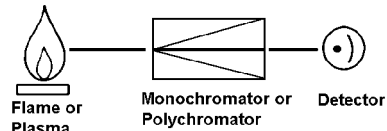
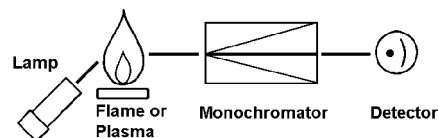
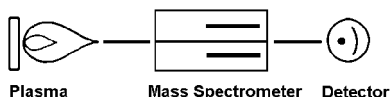
Atomic Absorption**Atomic Emission****Atomic Fluorescence****Atomic Mass Spectrometry**

Figure 1-3. Atomic spectroscopy systems.

containing free atoms and ions of the element of interest. Figure 1-3 shows the instrumental arrangements for four different techniques used to detect these atoms or ions.

In *atomic absorption spectroscopy* (AAS), light of a wavelength characteristic of the element of interest is shone through this atomic vapor. Some of this light is then absorbed by the atoms of that element. The amount of light that is absorbed by these atoms is then measured and used to determine the concentration of that element in the sample.

In *optical emission spectroscopy* (OES), the sample is subjected to temperatures high enough to cause not only dissociation into atoms but to cause significant amounts of collisional excitation (and ionization) of the sample atoms to take place. Once the atoms or ions are in their excited states, they can decay to lower states through thermal or radiative (emission) energy transitions. In OES, the intensity of the light emitted at specific wavelengths is measured and used to determine the concentrations of the elements of interest.

One of the most important advantages of OES results from the excitation properties of the high temperature sources used in OES. These thermal excitation sources can populate a large number of different energy levels for several different elements at the same time. All of the excited atoms and ions can then emit their characteristic radiation at nearly the same time. This results in the flexibility to choose from several different emission wavelengths for an element and in the ability to measure emission from several different elements concurrently. However, a disadvantage associated with this feature is that as the number of emission wavelengths increases, the

probability also increases for interferences that may arise from emission lines that are too close in wavelength to be measured separately.

In *atomic fluorescence spectrometry* (AFS), a light source, such as that used for AAS, is used to excite atoms only of the element of interest through radiative absorption transitions. When these selectively excited atoms decay through radiative transitions to lower levels, their emission is measured to determine concentration, much the same as in OES. The selective excitation of the AFS technique can lead to fewer spectral interferences than in OES. However, it is difficult to detect a large number of elements in a single run using AFS, as the number of spectral excitation sources and detectors that can be used at one time is limited by the instrument.

Another technique, called *atomic mass spectrometry*, is related to three atomic spectroscopy techniques described above. Instead of measuring the absorption, emission or fluorescence of radiation from a high temperature source, such as a flame or plasma, mass spectrometry measures the number of singly charged ions from the elemental species within a sample. Similar to the function of a monochromator in emission/absorption spectrometry that separates light according to wavelength, a quadrupole mass spectrometer separates the ions of various elements according to their mass-to-charge ratio in atomic mass spectrometry.

Atomization and Excitation Sources

In general, there are three types of thermal sources normally used in analytical atomic spectrometry to dissociate sample molecules into free atoms: flames, furnaces and electrical discharges. High-power lasers have also been used for this purpose but tend to be better suited for other uses such as solids sampling for other atomization sources.

The first two types of sources, flames and furnaces, are hot enough to dissociate most types of molecules into free atoms. The main exceptions are refractory carbides and oxides, which can exist as molecules at the upper flame and furnace temperatures of 3000 - 4000 °K. When configured properly, flames and furnaces can also be used to excite many elements for emission spectrometry. Because most of the free atoms in typical flames and furnaces are in their ground states, however, absorption spectrometry is the preferred method to detect the presence of elements of interest. The exceptions are those elements whose lowest excited state is low enough in energy that it can be easily populated by a flame or furnace. Examples of such elements are lithium, sodium and potassium. In fact, flame emission spectrometry is still widely regarded as the preferred method for detecting the alkali elements.

Electrical discharges are the third type of atomization sources used in analytical optical emission spectrometry. For many years, dc arcs and ac sparks were the mainstay of OES. These electrical discharges are created by applied currents or potentials across an electrode in an inert gas and typically produce higher temperatures than traditional flame systems.

More recently, other types of discharges, namely plasmas, have been used as atomization/excitation sources for OES. Strictly speaking, a plasma is any form of matter that contains an appreciable fraction ($>1\%$) of electrons and positive ions in addition to neutral atoms, radicals and molecules. Two characteristics of plasmas are that they can conduct electricity and are affected by a magnetic field.

The electrical plasmas used for analytical OES are highly energetic, ionized gases. They are usually produced in inert gases, although some work has also been done using reactive gases such as oxygen. These plasma discharges are considerably hotter than flames and furnaces and, thus, are used not only to dissociate almost any type of sample but also to excite and/or ionize the atoms for atomic and ionic emission. The present state-of-the-art in plasma sources for analytical optical emission spectrometry is the argon-supported inductively coupled plasma (ICP). Other plasmas currently being used include the direct current plasma (DCP) and the microwave induced plasma (MIP).

Because the argon ICP can efficiently generate singly charged ions from the elemental species within a sample, it makes an ideal ion source to use synergistically with mass spectrometers. This combination of an ICP and mass spectrometer is called ICP-MS.

A Short History of Optical Emission Spectroscopy

Flames and electrical discharges have been an important part of chemical analysis for a long time. In 1752, 26-year old Thomas Melville of Glasgow wrote of his observations of a bright yellow light emitted from a flame produced by burning a mixture of alcohol and sea salt. When the alcohol contained no salt, the yellow color disappeared. It has been said that if Melville had not died a year later, spectrochemical analysis might have gotten a much earlier start.

One of the first uses of sparks for chemical analysis was reported in 1776 by Alessandro Volta. Volta had discovered a way to produce a static electric charge strong enough to create sparks. He was fascinated by the different colors of sparks that he could obtain by sparking different materials. Eventually he was able to identify certain gases by the colors emitted when he applied a spark to them.

During the late 18th and early 19th centuries Fraunhofer and others looked at spectra emitted by flames and sparks, often comparing them to spectra emitted from the sun and planets. In 1826, W. H. Talbot reported a series of experiments in which he observed the coloring of flames by a variety of salts. Unfortunately, the utility of his work was not recognized for several decades.

It was not until 1859, when Kirchhoff and Bunsen surmised that the sharp line spectra from flames were produced by atoms and not molecules, that the nature of emission spectra was beginning to be understood. Much of their work was made possible by Bunsen's development of a burner which produced a nearly transparent, nonluminescent flame. This is the same burner that practically every chemist since Bunsen has used at one time or another. Credited with the discovery of spectrochemical analysis, Kirchhoff and Bunsen developed methods based on emission spectroscopy that led to the discovery of four elements, Cs, Rb, Tl, and In, between 1860 and 1864.

In the beginning of the 20th century, the sharp lines that appeared in the light emitted from electrical arcs and sparks were a driving force for science. These atomic lines were used to define the discrete energy levels that exist in atoms and were thus one major test of theories developed with quantum mechanics. The lines were also used analytically for qualitative analysis. Indeed, the appearance of sharp spectral lines that had not been previously observed was the proof that most scientists required for the verification of the discovery of a new element.

During the middle of the 20th century, quantitative arc and spark spectroscopy was the best tool that analysts had to probe trace concentrations for a wide range of elements. The sample preparation techniques used were, for many samples, difficult and/or time-consuming. Conductive solids were relatively easy to handle; they were simply machined into electrodes that could be used to support the electrical discharge. Liquid samples, however, had to be either dried or plated onto electrodes by various means. Nonconductive solid samples were mixed with a conductive matrix, usually graphite, and pressed into the end of a graphite electrode. In addition to difficulty in handling all but the conductive solid samples, the quality of the data obtained was not very good. Precision of analysis of 5 to 10% RSD was typical for a very good and careful analyst. Standards and samples had to be made very similar since effects arising from the composition of the sample matrix were often large and difficult to predict. This type of analysis is still used today in foundries where the samples can be made easily into electrodes, the range of sample concentrations is limited, and a library of matched standard materials already exists.

While arc/spark emission techniques enjoyed widespread popularity for the determination of metals, flame emission spectrometry, also known as flame photometry, was used extensively for determination of the alkalis and other easily excited

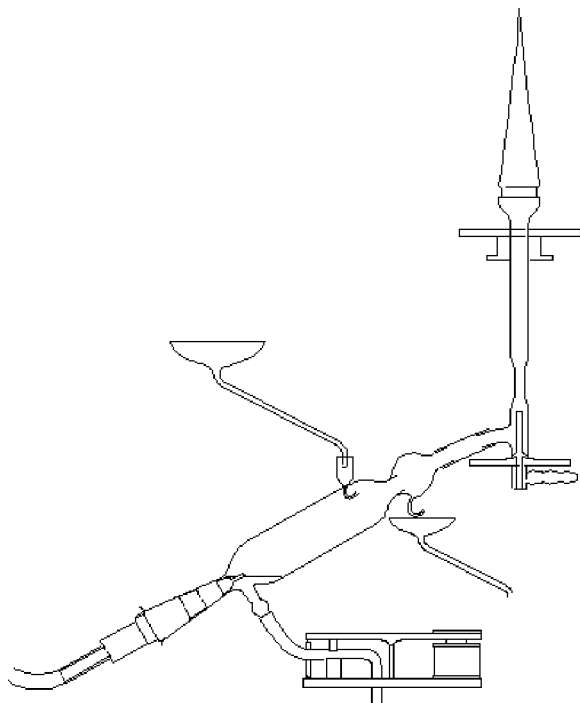


Figure 1-4. Spray chamber, nebulizer and burner such as those used by Lundegårdh for flame emission spectrography. (Used with permission from the Division of Analytical Chemistry of the American Chemical Society.)

elements. A Swedish agronomist named Lundegårdh is credited with beginning the modern era of flame photometry in the late 1920's. His apparatus for elemental analyses of plants, shown in Figure 1-4, used pneumatic nebulization and a premixed air-acetylene flame and is remarkably similar to equipment used today.

While the atomic spectra emitted from flames had the advantage of being simpler than those emitted from arcs and sparks, the main limitation of the technique was that the flames were not hot enough to cause emission for many elements. Despite that limitation, several successful commercial instruments were based on the technique, many of which are still in use today. The most widespread use of the

technique is in clinical labs for determining sodium and potassium levels in blood and other biological materials.

In the 1960's and 1970's both flame and arc/spark optical emission spectrometry declined in popularity. Many of the analyses that had been performed using optical emission were increasingly performed using atomic absorption spectrophotometry (AAS). While advances in flame emission spectrometry allowed the determination of about half of the elements in the periodic table, the technique could no longer compete well with AAS. Since absorption of light by ground state atoms was used as the mode of detection, the need for very high temperatures to populate excited states of atoms was no longer a limitation. The instabilities and spectral interferences which plagued arc/spark emission techniques were also greatly reduced by atomic absorption techniques.

At the time of its greatest popularity, flame atomic absorption was used primarily in the analysis of solutions for trace metals. For solid samples, the technique requires that samples be dissolved. With the exception of a few well-documented interferences, samples and standards need not be made very similar. Flame atomic absorption offers the analyst high precision (0.2 to 0.5% RSD) determinations and moderate detection limits. Electrothermal atomization (graphite furnace) atomic absorption spectrometry, on the other hand, offers high sensitivity and low detection limits. Graphite furnace AAS (GFAAS) does provide poorer precision and a higher level of matrix interferences than are experienced with the flame-based technique. However, advances such as the use of stabilized temperature platform furnace (STPF) technology and Zeeman background correction have reduced or eliminated most of the interferences previously associated with GFAAS.

Both the flame and graphite furnace AAS techniques are used widely today and both provide excellent means of trace elemental analysis. Most atomic absorption instruments are limited, however, in that they typically measure only one element at a time. The instrumental setup or operating conditions may require changing hollow cathode lamps or using different furnace parameters for each element to be determined. Because of the different operating conditions and furnace parameters required for each element, conventional atomic absorption techniques do not lend themselves readily to multi-element simultaneous analysis.

Also, despite advances in nonlinear calibration, the need for sample dilution is greater than for present-day OES techniques, due to the limited working (calibration) range for the AAS techniques. Consequently, devices for automatic sample dilution when a sample concentration exceeds the calibration range are available. For those samples that require element preconcentration for lower detection limits, flow-injection techniques coupled with cold vapor mercury or hydride generation equipment and GFAAS can not only provide significant improvements in detection limits, over 100 times better as compared to conventional hydride generation AA, but also may reduce potential interferences by the complete removal of matrix components.

Stanley Greenfield of Birmingham, England is credited with the first published report (1964) on the use of an atmospheric pressure inductively coupled plasma (ICP) for elemental analysis via optical emission spectrometry (OES) [1]. The conclusions from this landmark paper summarize what Greenfield identified as the advantages of plasma emission sources over flames, ac sparks and dc arcs:

The plasma source has a high degree of stability, has the ability to overcome depressive interference effects caused by formation of stable compounds, is capable of exciting several elements that are not excited in orthodox chemical flames, and gives increased sensitivity of detection [over flame photometry].

The plasma source is far simpler to operate than the conventional arc and spark methods, especially in solution and liquid analysis, and gives the high degree of stability associated with the a.c. spark combined with the sensitivity of the d.c. arc. Particular advantages of the high-frequency plasma torch are the lack of electrodes, which gives freedom from contamination, and the extremely low background produced.

As with most new techniques, the original optical emission results using ICP sources were not spectacular. The technique was better than flame atomic absorption for only a few of the most refractory elements. Along with Greenfield, Velmer Fassel and his colleagues at Iowa State University are generally credited with the early refinements in the ICP that made it practical for analysis of nebulized solutions by OES. The technique continued to be refined as sources of noise were tracked down and eliminated, and gas flows, torch designs and plasma settings were optimized. By 1973, the low detection limits, freedom from interferences and long linear working ranges obtained with the ICP proved that it was clearly an emission source superior to those used previously in analytical optical emission spectrometry. Since that time, an ever-increasing number of academic, governmental and industrial researchers have joined in the development of the ICP.

It has been mentioned that an affiliated technique to atomic spectroscopy for elemental analysis is ICP-MS. Though ICP-MS is not the subject of this handbook on the concepts, instrumentation and techniques in optical emission spectrometry, ICP-MS has become an important tool for the analyst since its commercial introduction in 1983. ICP-MS was pioneered by just a few prominent laboratories: Iowa State University, Ames, Iowa; Sciex, a manufacturer's laboratory in Toronto, Canada; and several facilities in the U.K. including the University of Surrey, the British Geological Survey and a U.K. manufacturer. The technique features high sensitivity and excellent detection limits, equal to or better than GFAAS for most elements. The mass spectra are considerably simpler than the atomic emission spectra from the ICP but the mass spectra are complicated by mass interferences from molecular ions originating in the ICP. However, ICP-MS allows for the routine use of isotopic ratio and isotopic dilution measurements to assist in the solution of analytical problems. Furthermore, qualitative analysis can be rapidly performed by ICP-MS techniques.

2 GENERAL CHARACTERISTICS OF ICP-OES

A well-known analytical chemist in the 1930's once facetiously suggested that the ideal analytical laboratory would have a shelf with 92 bottles and in each bottle a reagent which specifically reacts with one of the then-known 92 elements. Although it is not quite what the chemist had in mind when he made that suggestion, modern ICP-OES instruments can nearly achieve that chemist's wish. Routine determinations of 70 elements can be made by ICP-OES at concentration levels below one milligram per liter. Figure 2-1 contains a periodic table representation of the elements that can be determined by ICP-OES along with their detection limits.

In this chapter, some of the general characteristics of ICP-OES are described with the goal of providing an overview of the ICP and how it is used as a source for optical emission spectrometry. Also included is information regarding the typical performance characteristics and figures of merit that can be expected of the technique. Finally, the role of ICP-OES instrumentation in the modern analytical laboratory is discussed briefly. More detailed information about ICP-OES instrumentation, methodology and applications is covered in subsequent chapters.

The ICP Discharge

The inductively coupled plasma discharge used today for optical emission spectrometry is very much the same in appearance as the one described by Velmer Fassel in the early 1970's. Argon gas is directed through a torch consisting of three concentric tubes made of quartz or some other suitable material, as shown in Figure 2-2. A copper coil, called the load coil, surrounds the top end of the torch and is connected to a radio frequency (RF) generator.

When RF power (typically 700 - 1500 watts) is applied to the load coil, an alternating current moves back and forth within the coil, or oscillates, at a rate corresponding to the frequency of the generator. In most ICP instruments this frequency is either 27 or 40 megahertz (MHz). This RF oscillation of the current in the coil causes RF electric and magnetic fields to be set up in the area at the top of the torch. With argon gas being swirled through the torch, a spark is applied to the gas causing some electrons to be stripped from their argon atoms. These electrons are then

| ICP-AES Detection Limits (µg/L) | | | | | | | | | | | | | | | | | |
|---------------------------------|------------|-----------|----------|-----------|---------|-----------|-----------|---------|----------|-----------|-----------|----------|-----------|-----------|-----------|----------|--|
| Li 0.3 | Be 0.1 | | | | | | | | | | | B 1 | C 40 | N na | | | |
| Na 3 | Mg 0.1 | | | | | | | | | | | Al 3 | Si 4 | P 30 | S 30 | Cl na | |
| K 20 | Ca 0.02 | Sc 0.3 | V 0.5 | Ti 0.5 | Cr 2 | Mn 0.4 | Fe 2 | Co 1 | Ni 5 | Cu 0.4 | Zn 1 | Ga 4 | Ge 20 | As 20 | Se 50 | Br na | |
| Rb 30 | Sr 0.06 | Y 0.3 | Nb 5 | Zr 0.8 | Mo 3 | | Ru 6 | Th 5 | Pd 3 | Ag 1 | Cd 1 | In 9 | Sn 30 | Sb 10 | Te 10 | I na | |
| Cs 10 | Ba 0.1 | La 1 | Hf 4 | Ta 15 | W 8 | Re 5 | Os 0.4 | Ir 5 | Pt 10 | Au 4 | Hg 1 | Tl 30 | Pb 10 | Bi 20 | | | |
| | | | | | | | | | | | | | | | | | |
| | | Ce 5 | Pr 1 | Nd 1 | | Sm 2 | Eu 0.1 | Gd 1 | Tb 2 | Dy 2 | Ho 0.4 | Er 1 | Tm 0.5 | Yb 0.3 | Lu 0.2 | | |
| | | Th 70 | | U 15 | | | | | | | | | | | | | |

Figure 2-1. Periodic table with ICP-OES detection limits (side-on viewing). All detection limits are reported as 3σ and were obtained on a Perkin-Elmer Optima 3000 under simultaneous multielement conditions with a side-viewed plasma. Detection limits using an axially-viewed plasma are typically improved by 5–10 times.

caught up in the magnetic field and accelerated by them. Adding energy to the electrons by the use of a coil in this manner is known as *inductive coupling*. These high-energy electrons in turn collide with other argon atoms, stripping off still more electrons. This collisional ionization of the argon gas continues in a chain reaction, breaking down the gas into a plasma consisting of argon atoms, electrons, and argon ions, forming what is known as an inductively coupled plasma (ICP) discharge. The ICP discharge is then sustained within the torch and load coil as RF energy is continually transferred to it through the inductive coupling process.

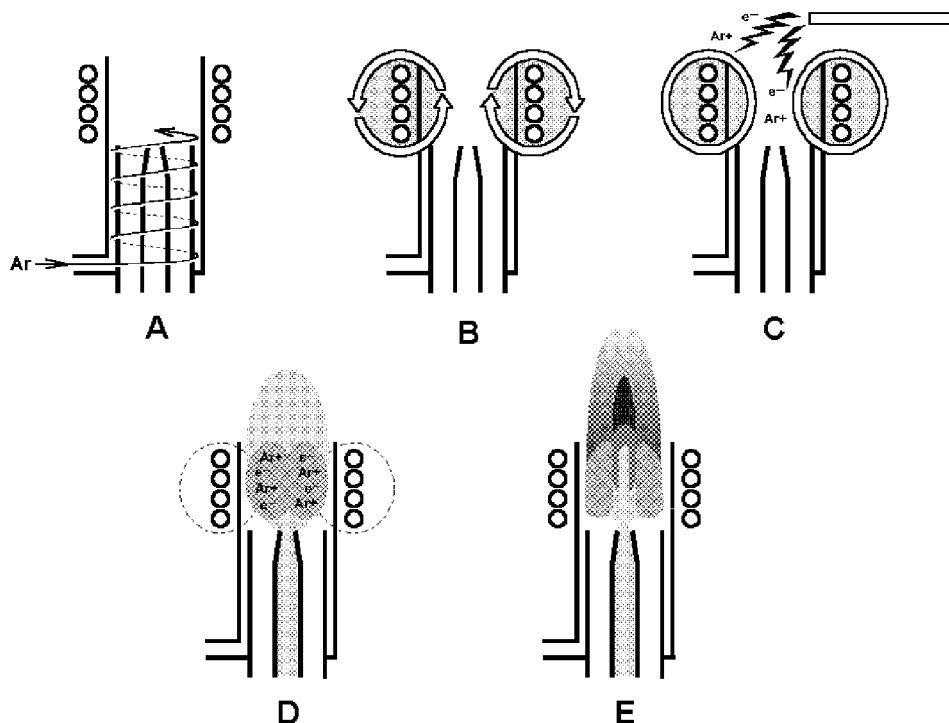


Figure 2-2. Cross section of an ICP torch and load coil depicting an ignition sequence. **A** - Argon gas is swirled through the torch. **B** - RF power is applied to the load coil. **C** - A spark produces some free electrons in the argon. **D** - The free electrons are accelerated by the RF fields causing further ionization and forming a plasma. **E** - The sample aerosol-carrying nebulizer flow punches a hole in the plasma.

The ICP discharge appears as a very intense, brilliant white, teardrop-shaped discharge. Figure 2-3 shows a cross-sectional representation of the discharge along with the nomenclature for different regions of the plasma as suggested by Koirtzmann *et al.* [2]. At the base, the discharge is toroidal, or "doughnut-shaped" because the sample-carrying nebulizer flow literally punches a hole through the center of the discharge. The body of the "doughnut" is called the induction region (IR) because this is the region in which the inductive energy transfer from the load coil to the plasma takes place. This is also the area from which most of the white light, called the argon continuum, is emitted. Allowing the sample to be introduced through the induction region and into the center of the plasma gives the ICP many of its unique analytical capabilities.

Most samples begin as liquids that are nebulized into an *aerosol*, a very fine mist of sample droplets, in order to be introduced into the ICP. The sample aerosol is then carried into the center of the plasma by the inner (or nebulizer) argon flow. The functions of the ICP discharge (hereafter referred to as the ICP or "the plasma") at this point are several fold. Figure 2-4 depicts the processes that take place when a sample droplet is introduced into an ICP.

The first function of the high temperature plasma is to remove the solvent from, or *desolvate*, the aerosol, usually leaving the sample as microscopic salt particles. The next steps involve decomposing the salt particles into a gas of individual molecules (*vaporization*) that are then dissociated into atoms (*atomization*). These processes, which occur predominantly in the preheating zone (PHZ) shown in Figure 2-3, are the same processes that take place in flames and furnaces used for atomic absorption spectrometry.

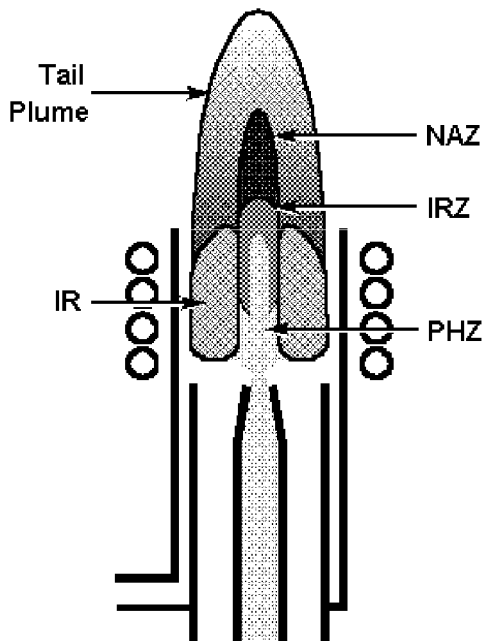


Figure 2-3. Zones of the ICP. IR - Induction Region, PHZ - Preheating Zone, IRZ - Initial Radiation Zone, NAZ - Normal Analytical Zone.

Once the sample aerosol has been desolvated, vaporized and atomized, the plasma has one, or possibly two, functions remaining. These functions are *excitation* and *ionization*. As explained in Chapter 1, in order for an atom or ion to emit its characteristic radiation, one of its electrons must be promoted to a higher energy level through an excitation process. Since many elements have their strongest emission lines emitted from the ICP by excited ions, the ionization process may also be necessary for some elements. The excitation and ionization processes occur predominantly in the initial radiation zone (IRZ) and the normal analytical zone (NAZ). The NAZ is the region of the plasma from which analyte emission is typically measured.

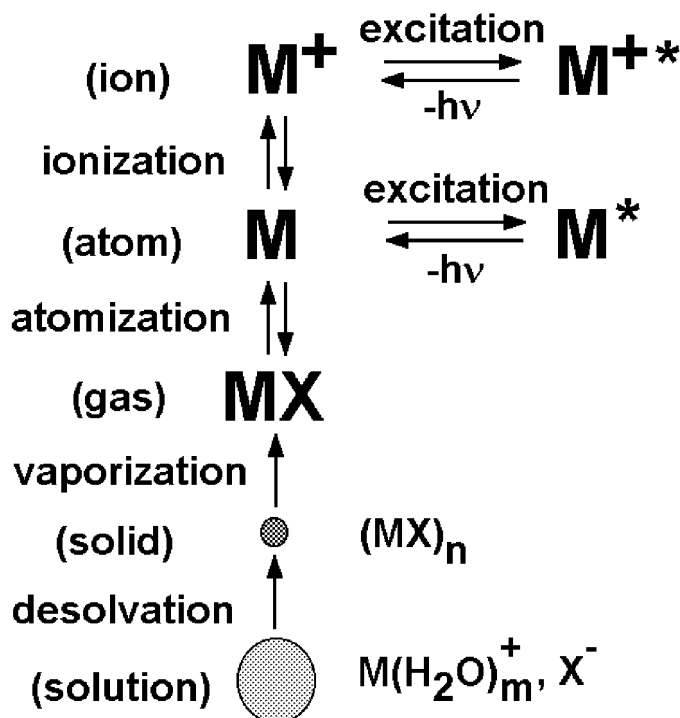


Figure 2-4. Process that takes place when a sample droplet is introduced into an ICP discharge.

While the exact mechanisms for excitation and ionization in the ICP are not yet fully understood, it is believed that most of the excitation and ionization in the ICP takes place as a result of collisions of analyte atoms with energetic electrons [3]. There is also some speculation about the role of argon ions in these processes. In any case, the chief analytical advantage of the ICP over other emission sources are derived from the ICP's ability to vaporize, atomize, excite, and ionize efficiently and reproducibly a wide range of elements present in many different sample types.

One of the important reasons for the superiority of the ICP over flames and furnaces for the above is in the high temperature within the plasma. Figure 2-5 shows approximate temperatures for different regions of the ICP. While flames and furnaces have upper temperature ranges in the area of 3300 K, the gas temperature in the center of the ICP is about 6800 K [4]. Besides improving excitation and

ionization efficiencies, the higher temperature of the ICP also reduces or eliminates many of the chemical interferences found in flames and furnaces.

Other electrical discharge emission sources, such as arcs, sparks, direct current plasmas, and microwave induced plasmas, also have high temperature and thus may be as efficient at excitation and ionization as the ICP. However, it is largely the ICP's combination of stability and freedom from sample matrix interferences that makes the ICP a better source for atomic emission spectrometry than these other electrical discharge sources.

An important feature of the ICP that is not common to most other emission sources is that since the sample aerosol is introduced through the center of the ICP, it can be surrounded by the high temperature plasma for a comparatively long time, approximately 2 milliseconds. It is this long residence time of the analyte particles in the center of the plasma that is largely responsible for the lack of matrix interferences in the ICP. In addition, because the aerosol is in the center of the discharge and the energy-supplying load coil surrounds the outside of the plasma, the aerosol does not interfere with the transfer of the energy from the load coil to the discharge. In some other sources, such as the direct current plasma, the sample travels around the outside of the discharge where it does not experience uniform high temperature for as long. In the arcs and sparks, the sample may commingle with the entire electrical discharge and interfere with the production and sustainment of the discharge. These situations lead to the higher levels of matrix effects and poorer stability that are often characteristic of non-ICP discharges.

Detection of Emission

In ICP-OES, the light emitted by the excited atoms and ions in the plasma is measured to obtain information about the sample. Because the excited species in the plasma emit light at several different wavelengths, the emission from the plasma is *polychromatic*. This polychromatic radiation must be separated into individual wavelengths so the emission from each excited species can be identified and its intensity can be measured without interference from emission at other wavelengths. The separation of light according to wavelength is generally done using a monochromator, which is used to measure light at one wavelength at a time, or a polychromator, which can be used to measure light at several different wavelengths at once. The actual detection of the light, once it has been separated from other wavelengths, is done using a photosensitive detector such as a photo-multiplier tube (PMT) or advanced detector techniques such as a charge-injection device (CID) or a charge-coupled device (CCD). Further details about monochromators, polychromators and detectors are included in Chapter 3.

Extraction of Information

Extracting qualitative and quantitative information about a sample using ICP-OES is generally straightforward. Obtaining *qualitative information*, *i.e.*, what elements are present in the sample, involves identifying the presence of emission at the wavelengths characteristic of the elements of interest. In general, at least three spectral lines of the element are examined to be sure that the observed emission can be indeed classified as that belonging to the element of interest. Occasional spectral line interferences from other elements may make one uncertain about the presence of an element in the plasma. Fortunately, the relatively large number of emission lines available for most elements allows one to overcome such interferences by choosing between several different emission lines for the element of interest. (Note: Qualitative analysis should only be attempted with ICPs utilizing a monochromator or advanced detector technology. Polychromators with photomultiplier detectors should not be used for qualitative analyses. Monochromators, polychromators and detectors are discussed in some detail in Chapter 3.)

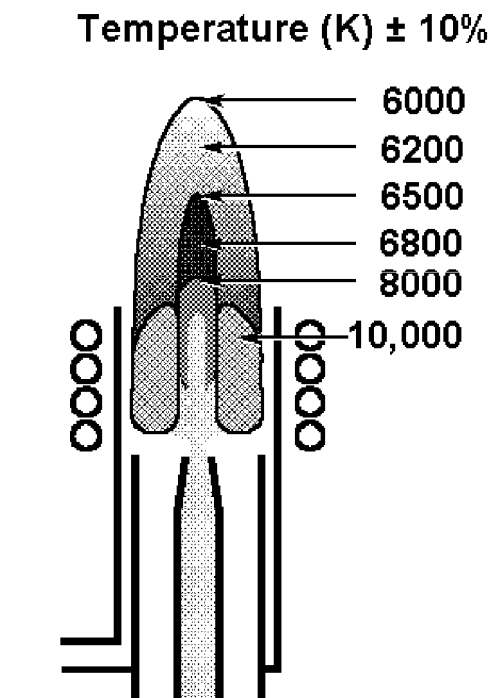


Figure 2-5. Temperature regions of a typical ICP discharge.

Obtaining *quantitative information*, *i.e.*, how much of an element is in the sample, can be accomplished using plots of emission intensity versus concentration called *calibration curves* (Figure 2-6). Solutions with known concentrations of the elements of interest, called *standard solutions*, are introduced into the ICP and the intensity of the characteristic emission for each element, or *analyte*, is measured. These intensities can then be plotted against the concentrations of the standards to form a calibration curve for each element. When the emission intensity from an analyte is measured, the intensity is checked against that element's calibration curve to determine the concentration corresponding to that intensity.

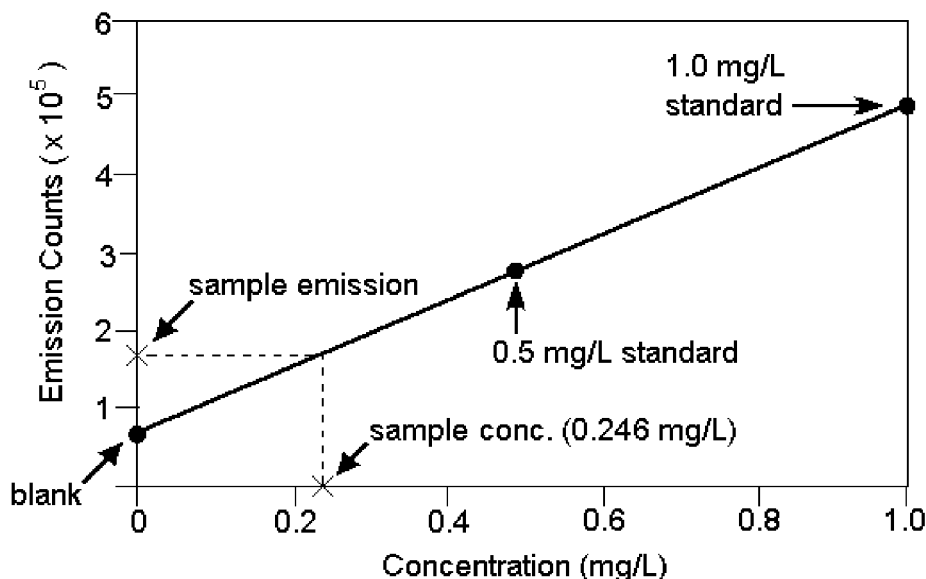


Figure 2-6. Calibration curve used for ICP-OES.

The computers and software used with ICP-OES instruments represent these calibration curves mathematically within the computer's memory. Thus, it is not necessary for the analyst to construct these curves manually for quantitation of the elements in the sample. Because calibration curves are generally linear over four to six orders of magnitude in ICP-OES, it is usually necessary to measure only one or two standard solutions, plus a blank solution, to calibrate the ICP instrument. In contrast to ICP-OES, arc and spark sources require five or more standards per element because of nonlinear calibration curves. The nonlinearity in these sources is a direct result of *self-absorption* which is the process by which some of the emitted radiation of the analyte is absorbed by ground state atoms in the plasma. In conventional ICPs, nonlinearity in the calibration curves is usually only observed for high analyte concentrations; *i.e.*, greater than 5 to 6 orders of magnitude above the detection limit. (The effect of self-absorption with regard to an axial or end-on ICP is discussed in Chapter 3.)

Performance Characteristics

As indicated in Figure 2-1, the ICP-OES technique is applicable to the determination of a large number of elements. The detection limits for these elements are generally in the $\mu\text{g/L}$ (ppb) range. As in many techniques, the detection limit is regarded as the lowest concentration at which the analyst can be relatively certain that an

element is present in a sample. Measurements made at or near the detection limit, however, are not considered to be quantitative. For purposes of rough quantitation ($\pm 10\%$), it is recommended that an element's concentration should be at least five times higher than the detection limit. For accurate quantitation ($\pm 2\%$), the concentration should be greater than 100 times the detection limit.

While most of the over 70 elements that can be determined by ICP-OES have low detection limits, it is worthwhile to discuss the elements that are usually not determined at trace levels by ICP-OES. These elements fall into three basic categories. The first category includes those elements that are naturally entrained into the plasma from sources other than the original sample. For example, in an argon ICP, it would be hopeless to try to determine traces of argon in a sample. A similar limitation might be encountered because of the CO_2 contamination often found in argon gas. When water is used as a solvent, H and O would be inappropriate elements, as would C if organic solvents were used. Entrainment of air into the plasma makes H, N, O and C determinations quite difficult, although not impossible.

Another category of elements generally not determined at trace levels by ICP-OES includes those elements whose atoms have very high excitation energy requirements such as the halogens, Cl, Br and I. Though these elements may be determined, the detection limits are quite poor compared to most ICP elements. The remaining category includes the man-made elements which are typically so radioactive or short-lived that gamma ray spectrometry is preferable for their determination.

The upper limit of linear calibration for ICP-OES is usually 10^4 to 10^6 times the detection limit for a particular emission line. For example, the maximum linear concentration for the Mn 257.610 nm emission line is about 50 mg/L or about 10^5 times its 0.0004 mg/L detection limit. The range of concentrations from the detection limit to this upper limit is known as the linear dynamic range (LDR) of the emission line.

The advantages of long LDRs are basically twofold. Firstly, it makes calibration of the instrument simpler. Atomic absorption, arc and spark techniques have LDRs of only one or two orders of magnitude and require the use of nonlinear calibration curves to extend the working range (*i.e.*, the actual calibration range used) for an element. While the techniques for calculating nonlinear curves have improved over the years, they still require multiple data points, *i.e.*, multiple standards must be run in order to define the nonlinear curve. In ICP-OES, where linear calibration curves are the norm, only two solutions, the blank and a high standard, need to be analyzed to produce a calibration curve.

The other advantage of long LDRs is that less sample dilution is required. Even when nonlinear curves are used, the techniques that have shorter LDR's tend to require more sample dilution to keep the analyte concentrations within the working range for the element of interest.

Besides being able to determine a large number of elements over a wide range of concentrations, a major advantage of the ICP-OES technique is that many elements can be determined easily in the same analytical run. This multielement capability arises from the fact that all of the emission signals needed to obtain qualitative and quantitative information are emitted from the plasma at the same time.

The precision and accuracy of the ICP-OES analyses are considered sufficient for most trace elemental analyses. Even in the presence of interferences, modern signal compensation techniques allow the analyst to perform analyses with remarkable accuracy. Precision of analysis is usually in the 1% or less RSD (relative standard deviation) range when the concentration is greater than 100 times the detection limit. Better precision can be obtained, but often with trade-offs in speed and/or flexibility, or through the use of longer measurement times and special signal compensation techniques.

When ICP-OES was first introduced as a technique for trace elemental analysis, it was claimed by some experts that the technique was free from interferences. While this was somewhat optimistic, the ICP-OES technique probably experiences the fewest interferences of any of the commonly used analytical atomic spectrometry techniques. Chemical interferences are largely eliminated by the high temperature of the plasma. Physical interferences can be compensated for easily by taking advantage of the ICP's multielement capability. While spectral interferences have the potential for causing the most inaccuracies with ICP-OES analyses, the use of high-resolution spectrometers and advanced background correction techniques, coupled with the flexibility to choose from many possible emission lines, allows for interference-free analyses of the majority of samples. The interferences mentioned above and methods for overcoming them will be described in greater detail in Chapter 4.

Role of the ICP in an Analytical Laboratory

The obvious role of the ICP-OES instrument is to determine the concentrations of certain elements in the samples of interest. There are, however, several instrumental alternatives to ICP-OES for trace elemental analysis. The analyst must, therefore, define their analytical goals, taking into careful consideration factors such as sample type, elements to be determined, sensitivity and speed of analysis required, sample volume, sample loads, cost, and a host of other factors before selecting a technique or combination of techniques.

In many laboratories, ICP-OES is used to complement the other techniques available in the lab. For example, many labs are equipped with an ICP-OES instrument to perform moderate sensitivity, high sample throughput, multielement analyses and a graphite furnace AAS instrument to perform single element determinations which require higher sensitivity. (In Chapter 3, the possibilities of replacing the single element GFAAS system with the axially viewed ICP is discussed.)

To provide a better understanding of the role of ICP-OES instruments in the modern analytical laboratory, the ICP-OES technique is compared to three other trace elemental analysis techniques—flame (FAAS) and graphite furnace (GFAAS) atomic absorption spectrometry and ICP-mass spectrometry (ICP-MS).

Flame and Furnace Atomic Absorption Spectrometries. The flame and furnace AAS techniques are both excellent choices for many analytical laboratories. Two principal advantages of FAAS are initial instrument cost and simplicity of operation. FAAS detection limits for many elements are comparable to those obtained by ICP-OES, although the ICP-OES technique is typically preferred for refractory compound-forming elements. The prices of the least expensive ICP-OES instruments are now approaching the prices of the top-of-the-line FAAS.

A principal advantage of the graphite furnace AAS technique over FAAS and ICP-OES is its greater sensitivity, which results in significantly lower detection limits for most elements. Another advantage of GFAAS is the ability to analyze very small amounts (μL) of sample easily. A low-cost GFAAS instrument is less expensive than ICP-OES instruments while top-of-the-line GFAAS instruments are in the same price range as the lower-to mid-priced ICP-OES instruments.

The main advantage of ICP-OES over the AAS techniques in general are its multielement capabilities, longer linear dynamic ranges, and fewer condensed phase interferences. In addition, besides the refractory compound-forming elements, elements such as I, P and S are detected with more sensitivity by the ICP-OES technique.

Inductively Coupled Plasma - Mass Spectrometry is one of the most recently developed techniques for trace elemental analysis. ICP-MS uses the same type of ICP source as is used for ICP-OES. In the ICP-MS technique, the analyte ions formed in the ICP are sent through a mass spectrometer where they are separated according to their mass/charge ratios (m/e). The number of ions at the m/e 's of interest are then measured and the results used for qualitative and quantitative purposes.

Since its commercial introduction in 1983, ICP-MS has been demonstrated to be a powerful trace elemental analysis technique. It has the sensitivity and detection

limits typical of GFAAS, combined with the multielement capability of ICP-OES. While mass spectral interferences are few, ones that do exist generally can be overcome by using alternate masses or mathematical correction techniques. Early ICP-MS systems, in addition to being much more expensive than ICP-OES instruments, have experienced more severe sample matrix interferences than are experienced in ICP-OES. However, these interferences, along with the cost of the instruments, have been considerably reduced through refinements in the instrumentation, particularly in the sample introduction system.

Because of their respective advantages and disadvantages, selecting between the ICP-OES, FAAS, GFAAS, and ICP-MS techniques for a given set of circumstances is generally not a difficult task. For example, if an application requires single element trace analyses for relatively few samples or if initial cost is the most important factor, then FAAS is quite often the technique of choice. If an application requires very low detection limits for just a few elements, the GFAAS technique would probably be selected. If however, an application required very low detection limits for forty elements per sample, then ICP-MS would be a likely candidate. Likewise, if the application called for multielement analyses of samples in a complicated matrix or if a high sample throughput rate with moderate sensitivity was required, then ICP-OES might be the best choice.

Of course, there are many more criteria for selection of techniques than those mentioned in the examples given. In many labs, all four types of instruments, FAAS, GFAAS, ICP-OES, and ICP-MS are all used, each with its own set of applications.

3 ICP-OES INSTRUMENTATION

In inductively coupled plasma-optical emission spectrometry, the sample is usually transported into the instrument as a stream of liquid sample. Inside the instrument, the liquid is converted into an aerosol through a process known as *nebulization*. The sample aerosol is then transported to the plasma where it is desolvated, vaporized, atomized, and excited and/or ionized by the plasma (see Chapter 2). The excited atoms and ions emit their characteristic radiation which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration information for the analyst. A representation of the layout of a typical ICP-OES instrument is shown in Figure 3-1.

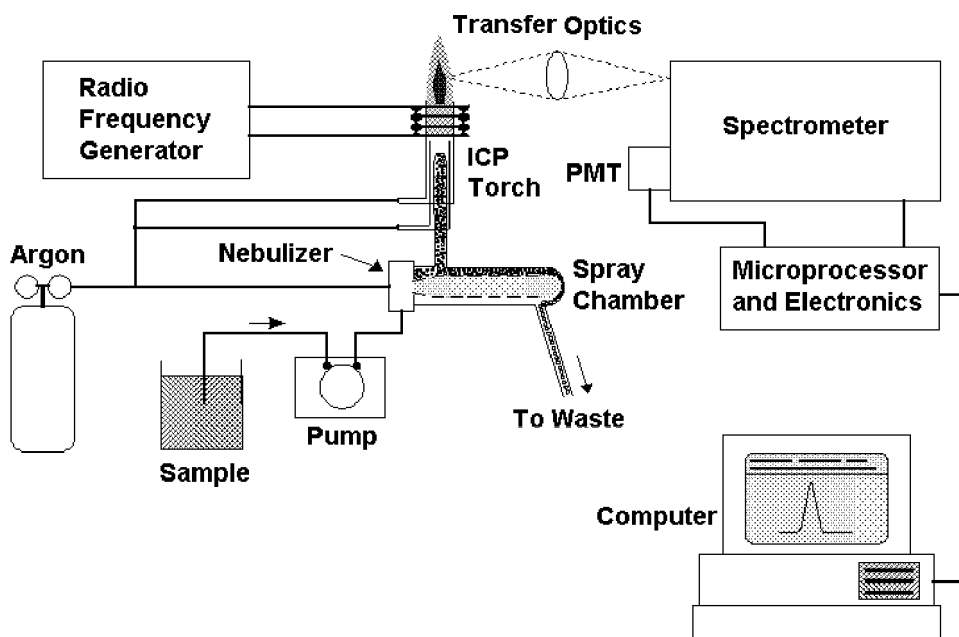


Figure 3-1. Major components and layout of a typical ICP-OES instrument.

In this chapter, the instrumentation used for each of these steps is described along with variations and alternatives that may be employed. The chapter is divided into sections dealing with the instrumentation for sample introduction, production of emission, collection and detection of emission, and signal processing and computer control. There is also a section briefly describing some of the accessories used with ICP-OES instruments.

SAMPLE INTRODUCTION

Nebulizers

Nebulizers are devices that convert a liquid into an aerosol that can be transported to the plasma. The nebulization process is one of the critical steps in ICP-OES. The ideal sample introduction system would be one that delivers all of the sample to the plasma in a form that the plasma could reproducibly desolvate, vaporize, atomize and ionize, and excite. Because only small droplets are useful in the ICP, the ability to produce small droplets for a wide variety of samples largely determines the utility of a nebulizer for ICP-OES.

Many forces can be used to break up a liquid into an aerosol; however, only two have been used successfully with an ICP, pneumatic forces and ultrasonic mechanical forces. Most commercial ICP nebulizers are of the pneumatic type. These nebulizers use high-speed gas flows to create an aerosol. The use of pneumatic nebulizers in ICP-OES follows their use and development in flame atomic absorption spectrometry, with one especially important difference in design considerations. In flame atomic absorption a gas flow on the order of ten liters per minute is often employed for nebulization, while the nebulization flow in the ICP is optimal at approximately one liter per minute. Years of research have left us with primarily three pneumatic nebulizers, each with its own advantages.

The type of pneumatic nebulizer most commonly used in flame AAS, and thus one of the first nebulizers to be used for ICP-OES, is the *concentric nebulizer*. A typical concentric nebulizer used for ICP-OES is shown in Figure 3-2. In this nebulizer, the solution is introduced through a capillary tube to a low-pressure region created by a gas flowing rapidly past the end of the capillary. The low pressure and high-speed gas combine to break up the solution into an aerosol.

The much lower sample aerosol carrier flow required for ICP spectrometry forced the designers of concentric pneumatic nebulizers to make the liquid and gas orifices much smaller than those common in flame spectrometers. With these small orifices, concentric pneumatic nebulizers can give excellent sensitivity and stability. However, the small orifices can be plagued by clogging problems, often by solutions containing as little as 0.1% dissolved solids. Advances in the design of concentric

nebulizers have improved their tolerance to dissolved solids with some being able to nebulize solutions containing 20% NaCl without clogging, for example. The most popular concentric nebulizers, the Meinhard® nebulizers, are made from glass and are therefore breakable and subject to corrosion by solutions containing hydrofluoric acid.

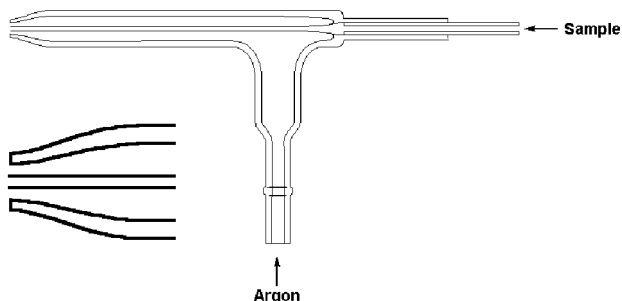


Figure 3-2. Concentric nebulizer used for ICP-OES.

Another type of concentric nebulizer, called the *micro-concentric nebulizer* (MCN), is also available (Figure 3-3). This compact nebulizer employs a small diameter capillary (polyimide or Teflon) and polyvinylidene difluoride (PVDF) body to minimize undesirable large drop formation and to facilitate HF tolerance. A very fine aerosol is produced consisting of only very small size droplets. While conventional concentric nebulizers have a sample uptake rate of 1 - 3 mL/min, the MCN is typically less than 0.1 mL/min permitting analysis of small sample volumes. This low sample uptake is beneficial in extending limited sample volumes so that the long nebuliza-

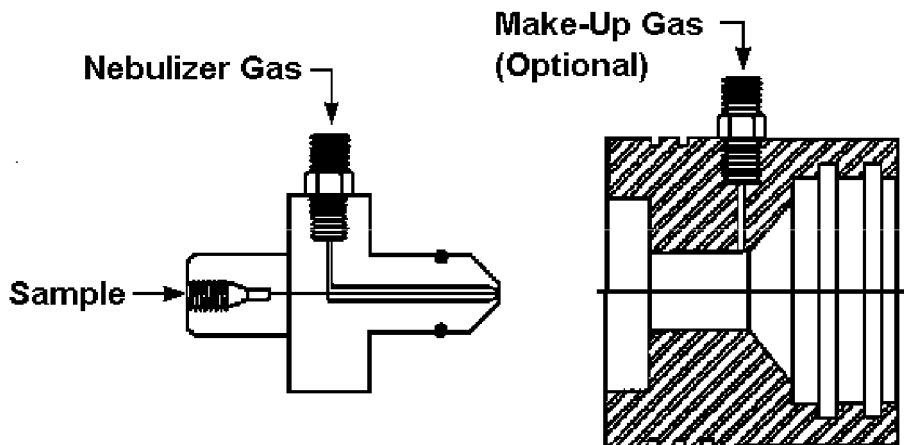


Figure 3-3. Micro-concentric nebulizer used for ICP-OES.

tion times encountered with sequential ICPs undertaking multielement analysis may be successfully accomplished. In addition to the small sample volume and low sample uptake rates, the nebulizer also exhibits fast washout times which may particularly critical for samples containing such elements as boron and mercury.

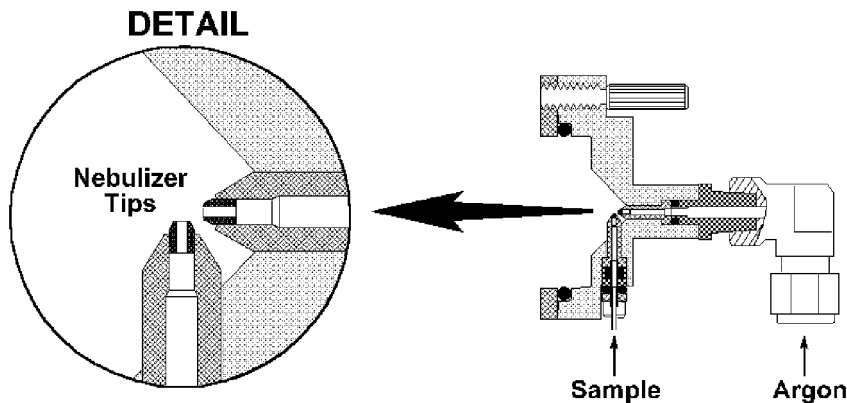


Figure 3-4. Cross-flow nebulizer.

A second type of pneumatic nebulizer is the *cross-flow nebulizer*, shown in Figure 3-4. The operation of cross-flow nebulizers is often compared to that of a perfume atomizer. Here a high speed stream of argon gas is directed perpendicular to the tip of a capillary tube (in contrast to the concentric or micro-concentric nebulizers where the high-speed gas is parallel to the capillary). The solution is either drawn up through the capillary tube by the low-pressure region created by the high-speed gas or forced up the tube with a pump. In either case, contact between the high-speed gas and the liquid stream causes the liquid to break up into an aerosol. Cross-flow nebulizers are generally not as efficient as concentric nebulizers at creating the small droplets needed for ICP analyses. However, the larger diameter liquid capillary and longer distance between liquid and gas injectors minimize clogging problems. Many analysts feel that the small penalty paid in analytical sensitivity is more than compensated for by the freedom from clogging. Another advantage of cross-flow nebulizers is that they are generally more rugged and corrosion-resistant than glass concentric nebulizers. In fact, this nebulizer is available with a Ryton body, a clear sapphire liquid capillary tip and a red ruby gas injector tip both contained in a polyetheretherketone (PEEK) body, all which provide chemical resistance to samples.

The third type of pneumatic nebulizer used for ICP-OES is the *Babington nebulizer*. This nebulizer was originally developed as a way to nebulize fuel oil for industrial burners. The Babington nebulizer, shown in Figure 3-5, works by allowing the liquid to flow over a smooth surface with a small hole in it. High-speed argon gas

Babington Nebulizer

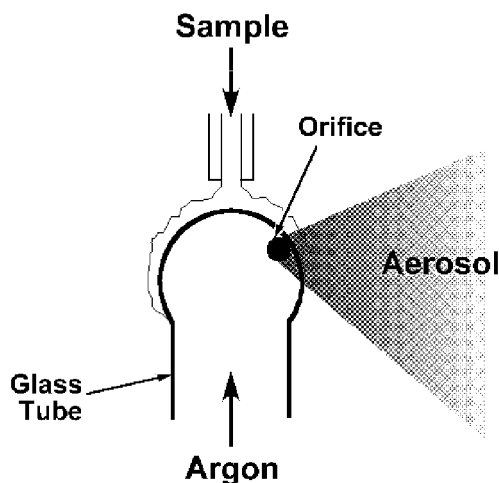


Figure 3-5. Babington nebulizer.

emanating from the hole shears the sheet of liquid into small drops. This nebulizer is the least susceptible to clogging and can nebulize very viscous liquids. A variation of the Babington nebulizer is the *V-groove nebulizer* shown in Figure 3-6. In the V-groove nebulizer, the sample flows down a groove which has a small hole in the center for the nebulizing gas. Working on the same principle as the Babington nebulizer, the V-groove nebulizer is being used increasingly for nebulization of solutions containing high salt and particulate concentrations. Improvements in the V-groove nebulizer include the cone spray nebulizer, shown in Figure 3-7, which is similar in principal to the V-groove but exhibits short term precisions of better than 1% for both aqueous solutions

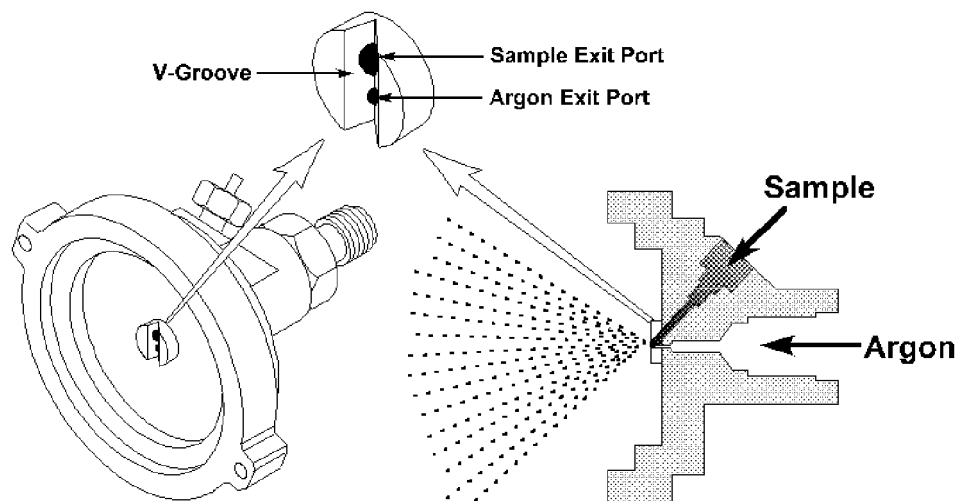


Figure 3-6. V-groove nebulizer, a variation of the Babington nebulizer.

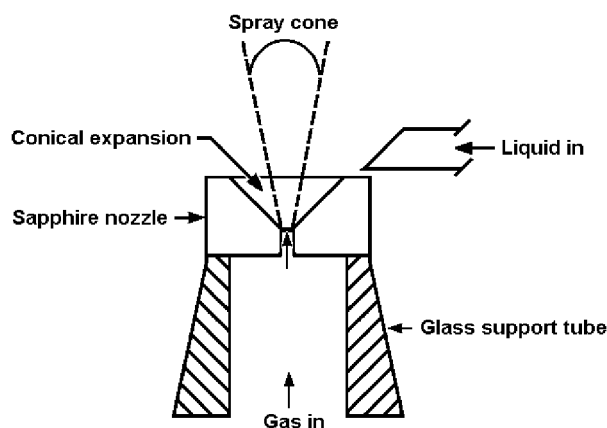


Figure 3-7. Conespray nebulizer, a modified Babington nebulizer.

and soil samples with high dissolved solids. Other names for the V-groove nebulizer include *modified Babington nebulizer*, *high solids nebulizer* and *maximum dissolved solids nebulizer*.

In *ultrasonic nebulization*, liquid sample is pumped onto an oscillating piezoelectric transducer. The oscillations break the sample into a fine aerosol, so aerosol formation is independent of nebulizer gas flow. The efficiency of an ultrasonic nebulizer is typically between 10% and 20%, at least 10-fold greater than typical pneumatic nebuliza-

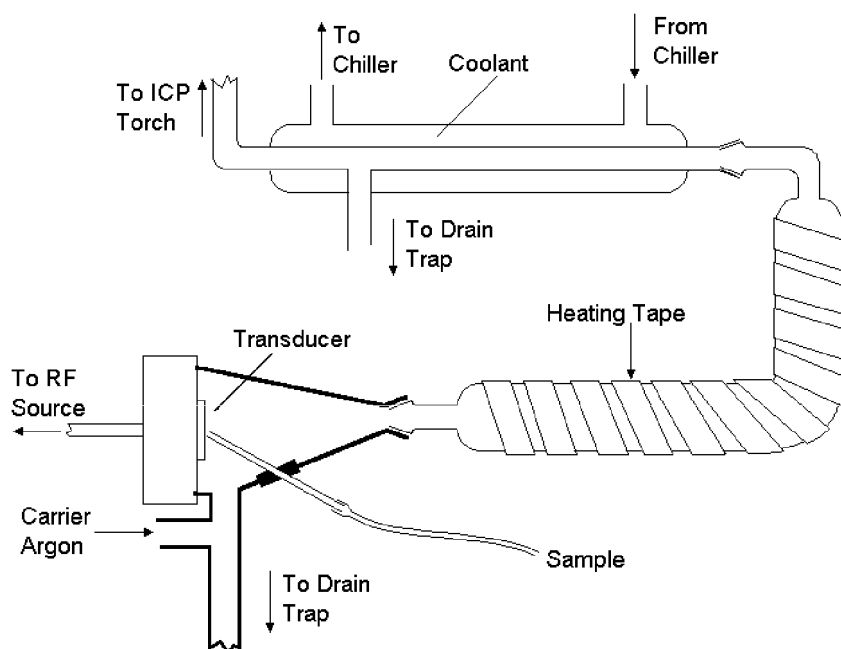


Figure 3-8. Ultrasonic nebulizer with desolvation unit.

tion. More sample will reach the ICP, providing detection limits which are usually 10 times lower than pneumatic nebulization. The higher efficiency of the ultrasonic nebulizer increases the water load to the ICP, so a desolvation unit is added after the nebulizer (Figure 3-8). The cooling portion of the desolvation unit has been replaced, in some commercially available systems, with a Peltier cooling device. New autotuning circuitry has greatly improved the short and long term stability of the ultrasonic nebulizer allowing the system to be used for routine work. However, the ultrasonic nebulizer is still susceptible to matrix effects, high solids loading and is not HF resistant.

Pumps

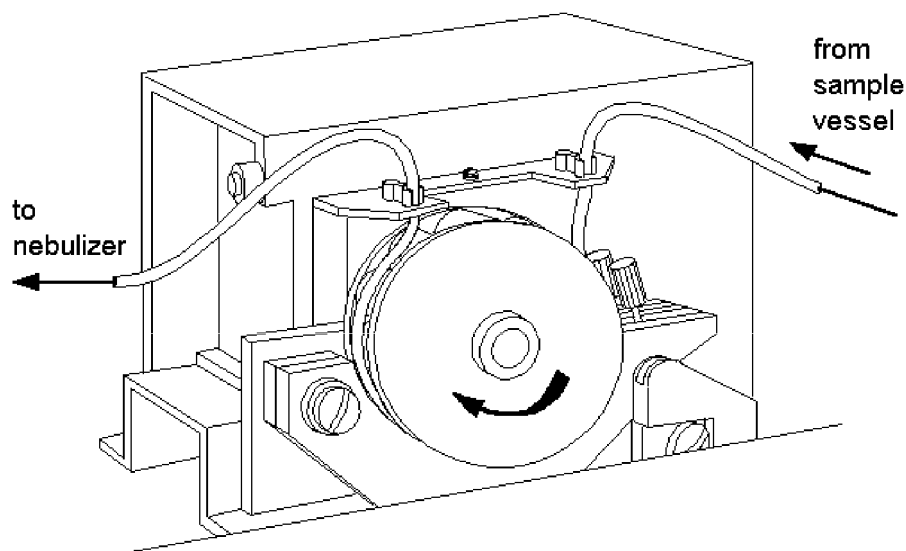


Figure 3-9. Peristaltic pump used for ICP-OES.

Some of the nebulizers discussed here require that the solution be pumped into the nebulizer, the Babington types, including the V-groove, and the ultrasonic. While the concentric and some cross-flow nebulizers can naturally draw the solution into the nebulizer by a process known as *aspiration*, a pumped flow is useful for these nebulizers also. With a pumped solution, the flow rate of the solution into the nebulizer is fixed and is not as dependent on solution parameters such as viscosity and surface tension. The controlled flow rate of liquid also allows for more rapid washout of the nebulizer and spray chamber.

Peristaltic pumps, such as the one shown in Figure 3-9, are almost exclusively the pumps of choice for ICP-OES applications. These pumps utilize a series of rollers

that push the sample solution through the tubing using a process known as peristalsis. The pump itself does not come in contact with the solution, only with the tubing that carries the solution from the sample vessel to the nebulizer. Thus, the potential for contamination of the solution that may exist with other types of pumps is not a concern.

The special tubing used with a peristaltic pump must be compatible with the sample that is passing through it. Most types of peristaltic pump tubing are compatible with weakly acidified aqueous media. Pumping strongly acidic solutions or organic solvents, however, usually requires the use of tubing made of specific materials. ICP-OES instrument Operator's Manuals often include guidelines for selection of the proper tubing. If this information is not provided, the analyst should consult chemical resistivity tables to select the proper pump tubing when strong acids or organic solvents are to be pumped.

Peristaltic pump tubing is the one part of an ICP system that usually requires frequent replacement. The analyst should check the pump tubing daily for wear, which is generally indicated by permanent depressions in the tubing that can be felt by running one's fingers over the tubing. Failure to replace the worn pump tubing can result in poor instrument performance, since this may prevent a steady stream of sample from being delivered to the nebulizer. Tubing wear can be reduced by releasing the tension on the tubing when the pump is not in use.

Spray chambers

Once the sample aerosol is created by the nebulizer, it must be transported to the torch so it can be injected into the plasma. Because only very small droplets in the aerosol are suitable for injection into the plasma, a *spray chamber* is placed between the nebulizer and the torch. Some typical ICP spray chamber designs are shown in Figure 3-10. The primary function of the spray chamber is to remove large droplets from the aerosol. A secondary purpose of the spray chamber is to smooth out pulses that occur during nebulization, often due to pumping of the solution.

In general, spray chambers for the ICP are designed to allow droplets with diameters of about 10 μm or smaller to pass to the plasma. With typical nebulizers, this droplet range constitutes about 1 - 5% of the sample that is introduced to the nebulizer. The remaining 95 - 99% of the sample is drained into a waste container. The material from which a spray chamber is constructed can be an important characteristic of a spray chamber. Spray chambers made from corrosion-resistant materials allow the analyst to introduce samples containing hydrofluoric acid which could damage glass spray chambers.

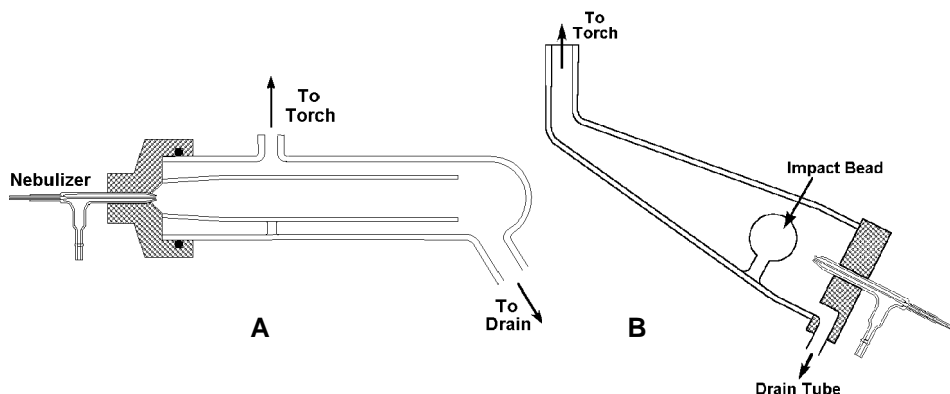


Figure 3-10. Typical spray chambers used with ICP-OES. **A** - Scott double pass type, **B** - conical single-pass type with impact bead.

Drains

While it is a seemingly simple part of a sample introduction system, the drain that carries excess sample from the spray chamber to a waste container can have an impact on the performance of the ICP instrument. Besides carrying away excess sample, the drain system provides the backpressure necessary to force the sample aerosol-carrying nebulizer gas flow through the torch's injector tube and into the plasma discharge. If the drain system does not drain evenly or if it allows bubbles to pass through it, the injection of sample into the plasma may be disrupted and noisy emission signals can result.

Drains for ICP-OES sample introduction systems come in many forms—loops, blocks, U-tubes, or even tubing connected to a peristaltic pump. For proper performance, it is important to keep the liquid level within the drain system at the recommended position. Also, when introducing organic-based samples into the ICP, it may be necessary to use drain tubing designated for use with organic solvents.

Alternative Sample Introduction Techniques

Several alternatives to nebulizers and spray chambers have been used as sample introduction systems for ICP-OES. The most widely used alternative technique is *hydride generation*. With this technique, the sample, in dilute acid, is mixed with a reducing agent, usually a solution of sodium borohydride in dilute sodium hydroxide. The reaction of the sodium borohydride with the acid produces atomic hydrogen. The atomic hydrogen then reacts with the Hg, Sb, As, Bi, Ge, Pb, Se, Te, and Sn in the solution to form volatile hydrides of these elements. These gaseous com-

pounds are then separated from the rest of the reaction mixture and transported to the plasma. A schematic representation of a continuous-flow hydride generation system is shown in Figure 3-11.

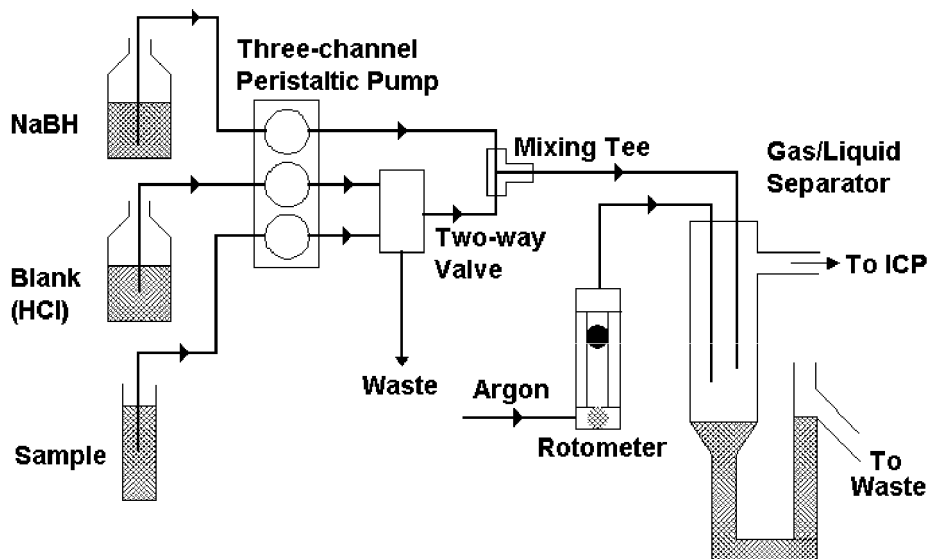


Figure 3-11. Schematic representation of a hydride generator.

Improvements in detection limits by a factor of up to 1000 for those elements listed above have been achieved using hydride generation. The reasons for the vast improvement in sensitivity for these elements are 1) the sample introduction rate for the hydride generator is often as much as ten times the rate for a pneumatic nebulizer, and 2) the efficiency with which the volatile hydrides are delivered to the plasma is near 100%, compared to the 1 - 5% efficiency when using a pneumatic nebulizer and spray chamber.

The graphite furnace or other electrothermal device has been used in research laboratories to vaporize a small portion of a liquid or solid sample for ICP-OES sample introduction. Most researchers have chosen to use one of the graphite tube atomizers designed for atomic absorption spectrometry. As shown in Figure 3-12, the normal sample introduction system of the ICP instrument is replaced by a graphite furnace. The sample vapor from the furnace is swept into the center of the ICP discharge in a conventional torch. While high sensitivity is possible, other aspects of using electrothermal vaporization, such as the use of compromise

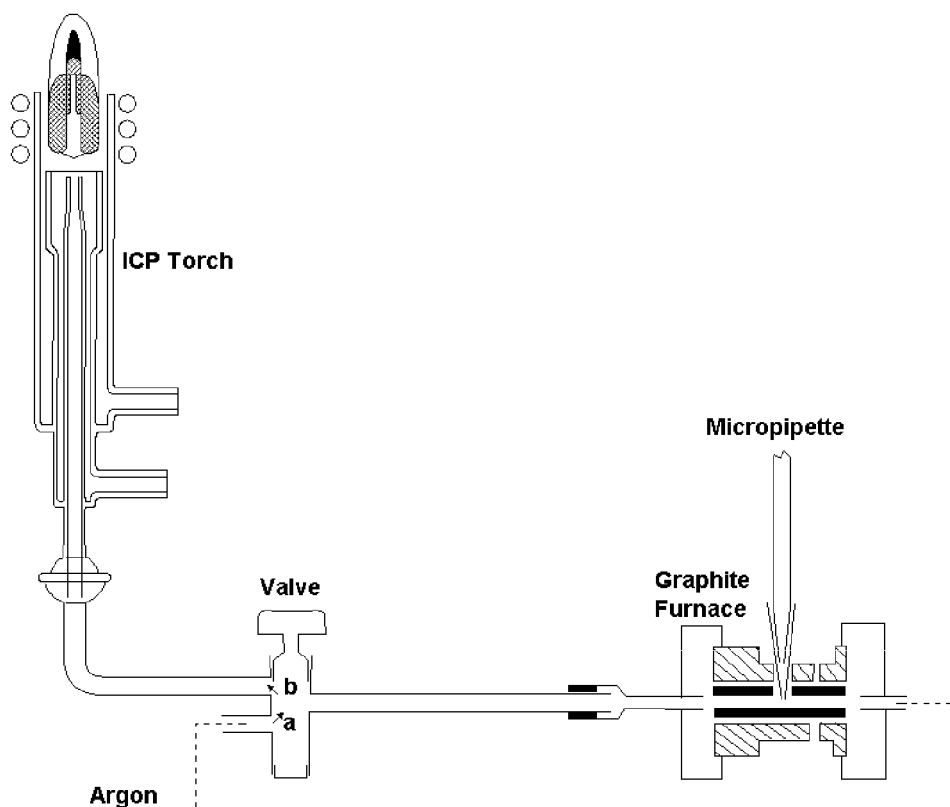


Figure 3-12. Graphite furnace modified for ICP-OES sample introduction.

furnace conditions, have limited the number of applications of this technique for ICP sample introduction. Also, since these devices are generally not of a continuous-flow nature, their use requires an ICP instrument that can record transient signals. The electrothermal vaporization devices have not met with much commercial success with ICP instrumentation but have realized some application as a sample introduction system for ICP-MS.

Solid samples have been introduced to the plasma via arc and spark sources such as those first used in the early days of optical emission spectrometry. Laser ablation techniques, in which a high-power laser is used to vaporize a small portion of a sample, have also been applied to the analysis of solids by ICP-OES. While a few applications using these techniques have been reported, the difficulty of stand-

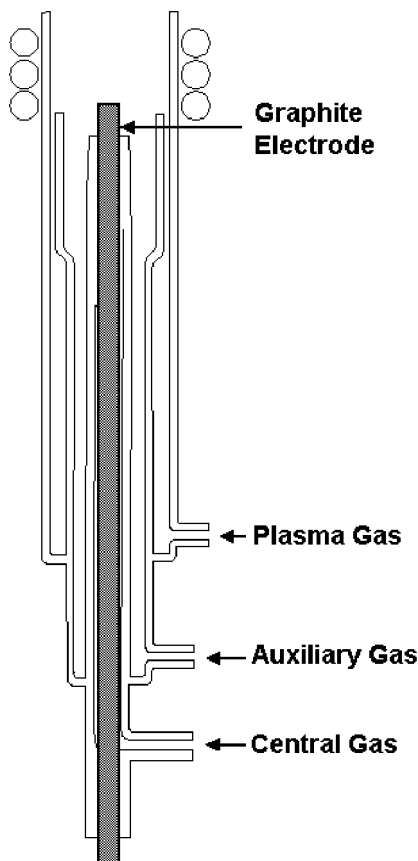


Figure 3-13. Direct insertion device.

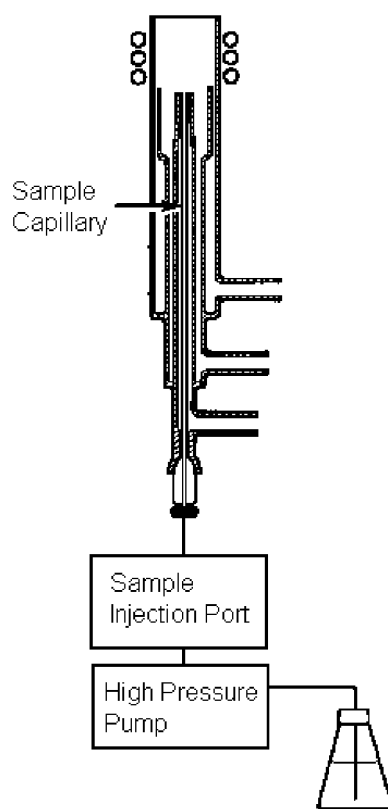


Figure 3-14. Direct injection nebulizer.

ardizing with solids can limit their utility in some cases. There are two major considerations in laser ablation, suitable matrix matched standards and the high cost, that have limited the use of this technique.

Some researchers have inserted solid samples directly into the center of the plasma toroid using a special device such as the one shown in Figure 3-13. This technique is referred to as *direct insertion*. A carbon electrode is packed with a solid sample and inserted into the plasma. The sample vaporizes into the plasma and atomic emission can be observed. However, as yet, the direct insertion technique has not been commercialized.

Another technique, direct injection nebulization, uses a micro concentric nebulizer that is inserted into the ICP torch in place of the normal injector tube. Sample is sprayed directly into the central channel of the ICP; there is no spray chamber. This technique has been applied successfully to the determination of memory-prone elements (B, I and Hg), analyses of small volume samples enabling high sample throughput, and as an interface for on-line liquid chromatography. An important feature of the direct injection nebulizer (DIN), illustrated in Figure 3-14, is 100% sample transport efficiency so sample waste is minimized and analyte transport effects are eliminated.

The study of sample introduction techniques is an active area for ICP-related research. Because sample introduction has been referred to as the "Achilles' heel" of atomic spectrometry [5], scientists and engineers are continuously working to improve the current techniques as well as invent new ones. Once the sources of interferences are identified and remedied, techniques such as direct insertion and vapor phase sample introduction techniques may be useful for routine chemical analysis.

PRODUCTION OF EMISSION

Torches

The torches used today in ICP-OES are very similar in design and function to those reported by Fassel in the early days of ICP-OES [6]. As shown schematically in Figure 3-15, the torches contain three concentric tubes for argon flow and aerosol injection. The spacing between the two outer tubes is kept narrow so that the gas introduced between them emerges at high velocity. This outside chamber is also designed to make the gas spiral tangentially around the chamber as it proceeds upward. One of the functions of this gas is to keep the quartz walls of the torch cool

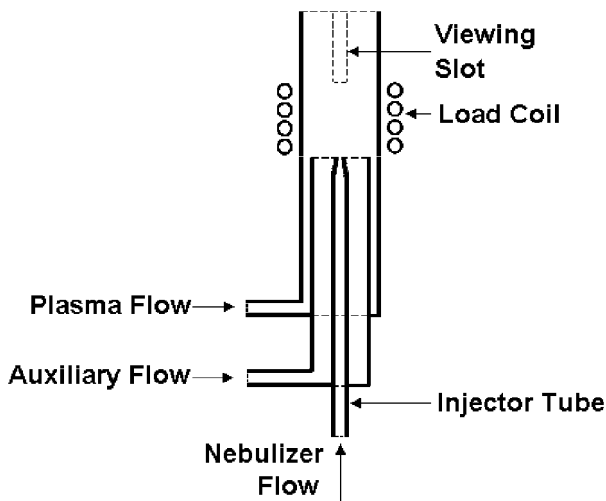


Figure 3-15. Schematic of a torch used for ICP-OES.

and thus this gas flow was originally called the *coolant flow* or *plasma flow* but is now called the "*outer*" gas flow. For argon ICPs, the outer gas flow is usually about 7 - 15 liters per minute.

The chamber between the outer flow and the inner flow sends gas directly under the plasma toroid. This flow keeps the plasma discharge away from the intermediate and injector tubes and makes sample aerosol introduction into the plasma easier. In normal operation of the torch, this flow, formerly called the *auxiliary flow* but now the *intermediate* gas flow, is about 1.0 L/min. The intermediate flow is usually introduced to reduce carbon formation on the tip of the injector tube when organic samples are being analyzed. However, it may also improve performance with aqueous samples as well. With some torch and sample introduction configurations, the intermediate flow may be as high as 2 or 3 L/min or not used at all.

The gas flow that carries the sample aerosol is injected into the plasma through the central tube or injector. Due to the small diameter at the end of the injector, the gas velocity is such that even the 1 L/min of argon used for nebulization can punch a hole through the plasma. Since this flow carries the sample to the plasma, it is often called the *sample* or *nebulizer flow* but in present terminology, this flow is known as the *inner gas flow*. Furthermore, this flow acts as the carrier gas for solid aerosols from spark ablation and laser ablation sample introduction techniques.

The "classic" ICP torch design is the one-piece torch shown in Figure 3-16. This torch consists of three concentric quartz tubes sealed together. While the need for permanently aligning the three tubes makes these torches more difficult to manufacture, they generally provide good plasma stability and are easy to use. The disadvantages of the one-piece torch are that 1) they are not resistant to corrosion by hydrofluoric acid, and 2) if the torch is damaged, usually the entire torch must be replaced.

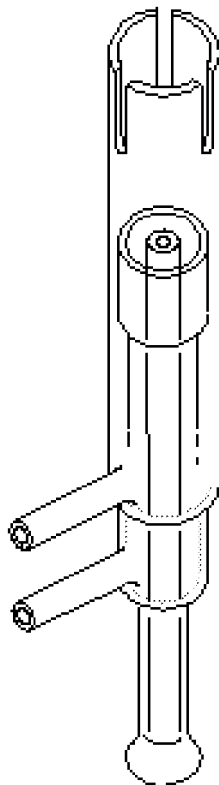


Figure 3-16. One-piece ICP torch.

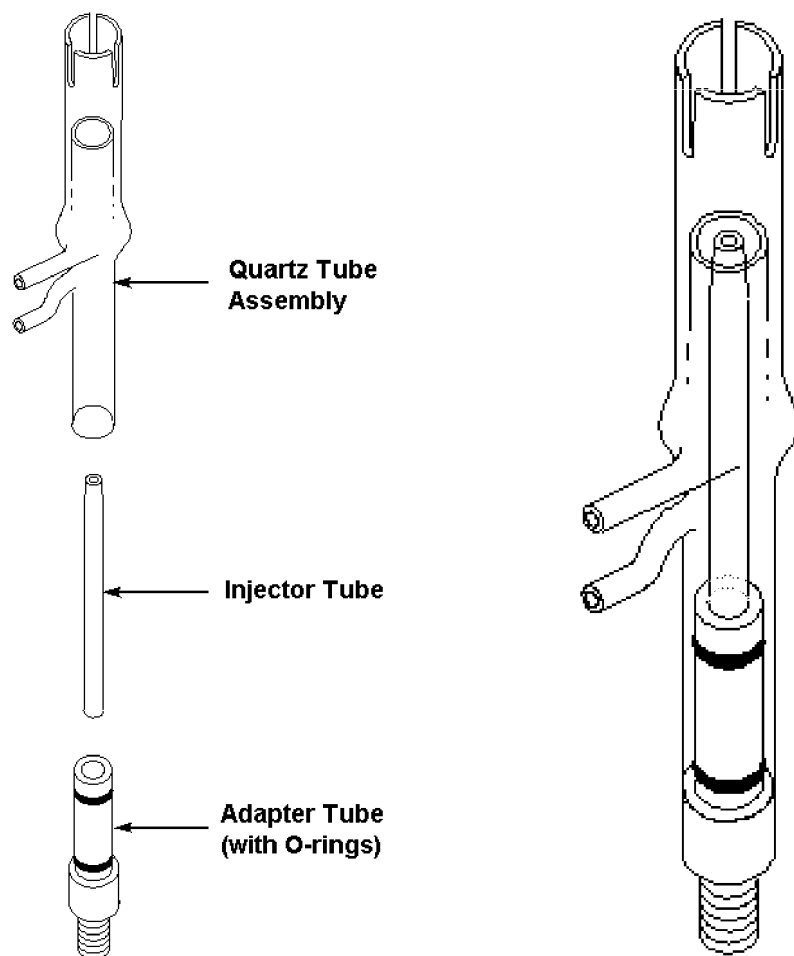


Figure 3-17. Demountable ICP Torch. **A** - expanded view, **B** - assembled view.

At present, the most popular torches are of the *demountable* type such as the one shown in Figure 3-17. These torches can be taken apart so that the tubes can be modified or replaced without replacing the entire torch. The main advantages of the demountable torch lie in the lower torch replacement costs and the ability to use a variety of injector tubes. Such injectors include corrosion-resistant ceramic injectors, narrow-bore injectors for analyses involving organic solvents, and wide-bore injectors for introducing samples with high dissolved solids contents.

Radio Frequency Generators

The radio frequency (RF) generator is the device that provides the power for the generation and sustainment of the plasma discharge. This power, typically ranging from about 700 to 1500 watts, is transferred to the plasma gas through a load coil surrounding the top of the torch. The load coil, which acts as an antenna to transfer the RF power to the plasma, is usually made from copper tubing and is cooled by water or gas during operation.

Most RF generators used for ICP-OES operate at a frequency between 27 and 56 MHz. The specific frequency used for an ICP-OES instrument is partially determined by those frequencies that the U. S. Federal Communications Commission (FCC) and similar agencies worldwide have designated for scientific and industrial use. Traditionally, most ICP generators were operated at 27.12 MHz. However, an increasing number of instruments now operate at 40.68 MHz because of improvements in coupling efficiency and reductions in background emission intensity realized at this frequency. Frequencies greater than 40 MHz also have been used but have not been as successful commercially.

There are two general types of RF generators used in ICP instruments. *Crystal-controlled generators* use a piezoelectric quartz crystal to produce an RF oscillating signal that is amplified by the generator before it is applied at the load coil. The proper electrical parameters, such as output impedance, needed to keep the generator operating efficiently are controlled by a matching network that utilizes manual or automatic (servomechanical) components. The speed and accuracy of this matching network are critical to the operation of this type of generator.

Free-running generators, on the other hand, operate at an oscillation frequency that is dependent not only on the electronic components of the generator circuitry but also on conditions within the plasma discharge. Recent advances in generator design have taken advantage of this dependency through the design of a free-running ICP generator that automatically adjusts the generator output power to compensate for certain changes in the plasma [7]. In addition, free-running generators can generally be made from simpler parts and are often smaller and less costly than crystal-controlled generators.

COLLECTION AND DETECTION OF EMISSION

Transfer Optics

The emission radiation from the region of the plasma known as the normal analytical zone (NAZ) is sampled for the spectrometric measurement. Until recently, the analytical zone was observed from the side of the plasma operating in a vertical

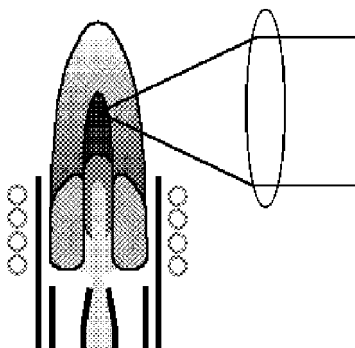


Figure 3-18. Side-on ICP Viewing.

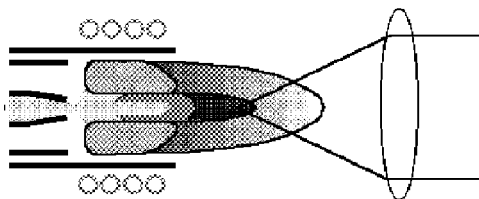


Figure 3-19. End-on ICP Viewing.

orientation as shown in Figure 3-18. This classical approach to ICP spectroscopy is referred to as a *radial or side-on viewing* of the plasma. In the early 1990's, a new "look" at the normal analytical zone of the ICP was commercialized. The plasma is rotated to a horizontal position and the zone is observed from the end of the plasma as illustrated in Figure 3-19. This configuration has become known as an *axial or end-on viewing* of the ICP. Recently, instruments that combine both *radial* and *axial* viewing, called *dual view*, have been introduced. The advantages associated with each of these configurations will be discussed on page 3-29.

No matter whether the ICP is a side-on or end-on viewing type configuration, the radiation is usually collected by a focusing optic such as a convex lens or a concave mirror. This optic then focuses the image of the plasma onto the entrance slit of the wavelength dispersing device or spectrometer. In some side-on configured instruments, the focusing optic is used in conjunction with mirrors that allow measurement of emission at different heights within the plasma. This viewing height adjustment makes the instrument more flexible, although it is not necessary for most analyses. (For end-on viewing ICPs, the ability to measure the emission at different heights is immaterial for most applications. However, the ability to adjust the mirror simplifies torch alignment.)

Conventional ICP Instrumentation

Wavelength Dispersive Devices. The next step in ICP-OES is the differentiation of the emission radiation from one element from the radiation emitted by other elements and molecules. The discrimination of this emission may be done in several

ways. The physical dispersion of the different wavelengths by a *diffraction grating* is by far the most common. Other devices less commonly used include prisms, filters and interferometers. Since, up to the early 1990's, most ICP-OES analyses were carried out using diffraction grating-based dispersive devices, the following discussion will be limited to more conventional instruments based on their use. (However, there is an additional wavelength dispersive device, called an *echelle grating*, that has become an important component in ICP instruments of the 1990's. Therefore, a separate section has been devoted to echelle gratings and instrument configurations designed around this component.)

A reflection diffraction grating is simply a mirror with closely spaced lines ruled or etched into its surface. Most gratings used in ICP-OES instruments have a line, or groove, density from 600 to 4200 lines per millimeter. When light strikes such a grating, it is diffracted at an angle that is dependent on the wavelength of the light and the line density of the grating. In general, the longer the wavelength and the higher the line density, the higher the angle of diffraction will be. Figure 3-20 shows schematically the paths that light rays of two different wavelengths would take when diffracted from a grating.

To separate polychromatic light predictably, the grating is incorporated in an optical instrument called a spectrometer. The function of the spectrometer is to form the light into a well-defined beam, disperse it according to wavelength with a grating, and focus the dispersed light onto an exit plane or circle. In other words, the spectrometer receives white light or polychromatic radiation and disperses it into monochromatic radiation. One or more exit slits on the exit plane or circle are then

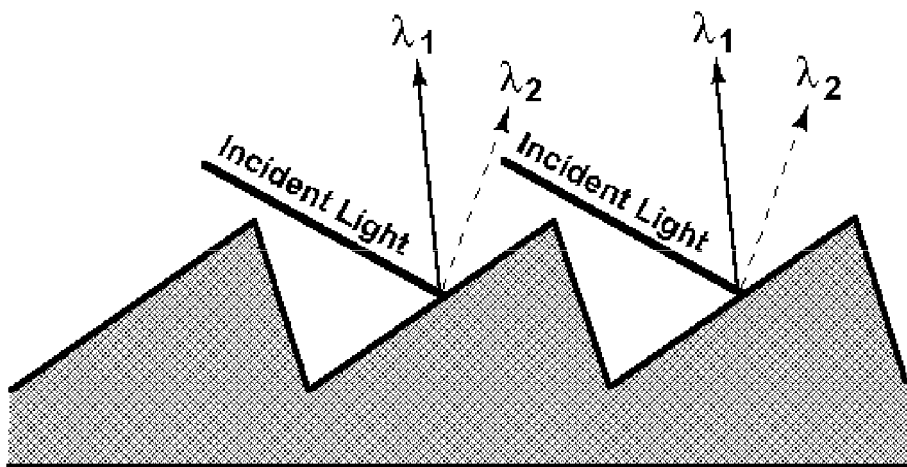


Figure 3-20. Diffraction grating separating two wavelengths of light.

used to allow certain wavelengths to pass to the detector while blocking out other wavelengths.

The monochromatic radiation which is diffracted from the grating is composed primarily of wavelengths representative of the light emitted by a particular elemental or molecular species in the ICP. But, not unlike musical instruments which produce harmonics of sound, the grating produces harmonics of light which are called *spectral orders*. For example, if the grating diffracts light with a wavelength of 200 nm, known as 1st order radiation, it is possible that radiation will be observed at 400 nm, a harmonic of the 200 nm light. This higher wavelength is known as a 2nd order line which is often designated as 2^o. In fact, a third harmonic of the 200 nm wavelength might be observed at 600 nm or 3rd order radiation (3^o).

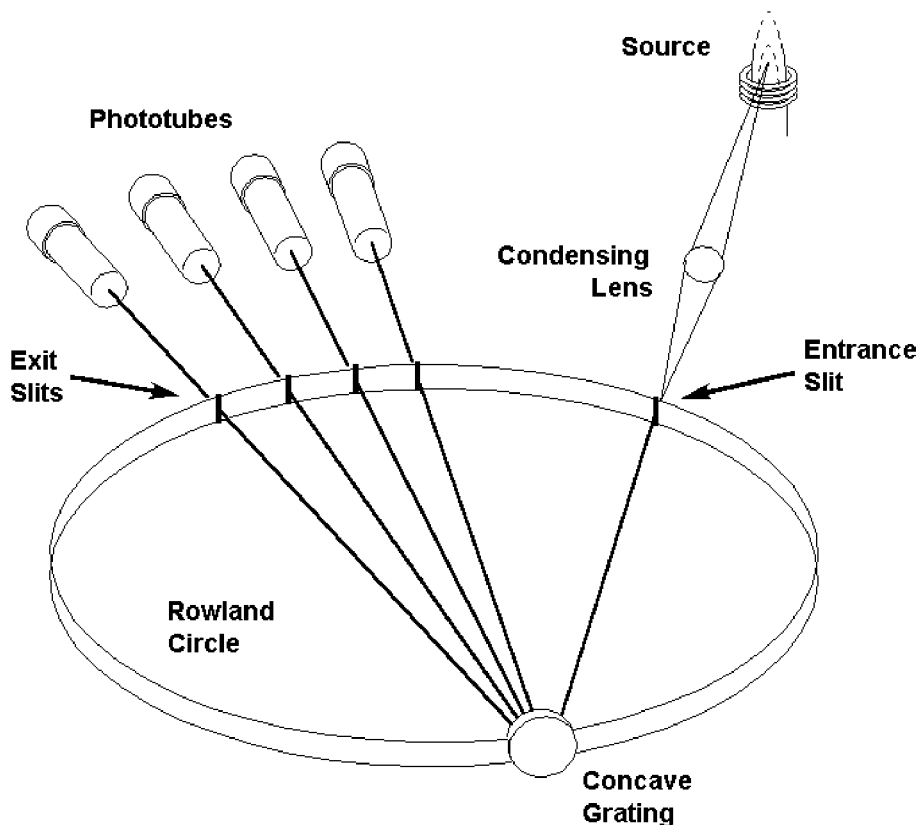


Figure 3-21. Paschen-Runge mount used in a Rowland circle polychromator.

Multielement analysis, the measurement of several elements from the same sample, is accomplished with conventional dispersive devices in two basic ways. When multiple exit slits and detectors are used in the same spectrometer, the device is called a *polychromator*. Each exit slit in a polychromator is aligned to an atomic or ionic emission line for a specific element to allow *simultaneous* multielement analyses. For conventional polychromators, the most popular design is the Paschen-Runge mount (Figure 3-21). This spectrometer consists of an entrance slit, a concave grating, and multiple exit slits, all on the periphery of what is known as a Rowland circle. (A newer instrumental approach to multielement analysis is presented on page 3-23.)

A *monochromator*, on the other hand, normally uses only one exit slit and detector. Monochromators are used in multielement analyses by scanning rapidly, or *slewing*, from one emission line to another. This is accomplished either by changing the angle of the diffraction grating by rotating it or by moving the detector in the exit plane of the monochromator while leaving the grating in a fixed position. When the monochromator slews between lines with sufficient speed, rapid *sequential* multielement analyses are possible. For conventional monochromators, the Czerny-Turner and Ebert mounts (Figure 3-22) dominate. These compact spectrometers have an entrance slit, a plane grating, either one (Ebert) or two (Czerny-Turner) mirrors for collimating and focusing the light, and a single exit slit.

Polychromator- and monochromator-based ICP-OES instruments each have their own relative advantages and disadvantages. With polychromators, each emission line can be observed during the entire sample introduction period, and theoretically,

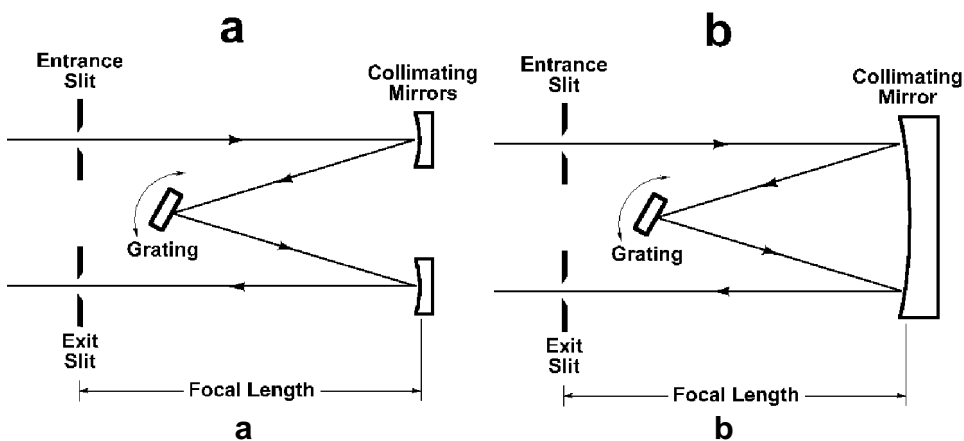


Figure 3-22. Czerny-Turner (a) and Ebert (b) monochromator mounts.

more samples can be analyzed in a shorter period of time. The same amount of time is required to determine five elements as it does thirty. Thus, polychromators have a high sample throughput rate. Because conventional polychromators contain an exit slit and PMT for each spectral line in the system, they are generally limited, because of space requirements, from 48 to 64 exit slits. However, most polychromators are programmed for 20 to 30 spectral lines.

Since the spectral line array for polychromators is fixed, spectral interference corrections may be applied to the analyte only if a spectral line for the element that is doing the interfering is included on the array. If a spectral line for the interfering line is not included, it may be necessary to disregard results for the particular analyte. (Interference effects will be discussed in more detail in Section 4.) Though it is possible to modify in the laboratory the spectral lines selection of the polychromator, it is generally difficult, time-consuming and expensive particularly for systems containing large numbers of exit slits.

The most important advantage of monochromator-based systems is their spectral flexibility. By this we mean the ability to access, at any time, any wavelength within the range of the monochromator. Clearly, the spectral flexibility of a monochromator-based ICP-OES instrument allows for the determination of any element whose emission can be measured by the technique. Also, because of their scanning capability, monochromator-based instruments are much better suited for application of the complex background correction techniques often necessary for ICP-OES. Furthermore, scanning the region around the analyte line or simultaneously measuring the immediate vicinity of the line assists in validating the analytical result. However, because elements are sequentially addressed, monochromators require large amounts of sample and have a lower sample throughput than polychromator systems. In general, for monochromators, if an analyte spectral line exhibits spectral interference, it is suggested to find an interference-free line.

Most of the analytically useful emission lines for ICP-OES are in the 190 - 450 nm region; thus, spectrometers used for ICP-OES are usually optimized for operation in this wavelength region. However, there are also some important ICP emission lines between 160 and 190 nm and above 450 nm. Unfortunately, electromagnetic radiation in the 160 - 190 nm wavelength region is readily absorbed by oxygen molecules, and instruments must be specially designed to remove the air from the spectrometer to observe emission in this wavelength region. Removing oxygen from the spectrometer is done either by *purging* the spectrometer with a gas, usually nitrogen or argon, that doesn't absorb the emission, or by removing the air from the spectrometer with a vacuum system. Recently, nitrogen filled optics maintained at atmospheric pressure and incorporating a catalyst for scrubbing the recycled nitrogen have been introduced.

Detectors. Once the proper emission line has been isolated by the spectrometer, the detector and its associated electronics are used to measure the intensity of the emission line. By far the most widely used detector for ICP-OES is the photomultiplier tube or PMT. (On page 3-25, modern, advanced detector systems based on charge transfer technology in silicon wafers will be discussed.)

The PMT is a vacuum tube that contains a photosensitive material, called the photocathode, that ejects electrons when it is struck by light. These ejected electrons are accelerated towards a dynode which ejects two to five secondary electrons for every one electron which strikes its surface. The secondary electrons strike another dynode, ejecting more electrons which strike yet another dynode, causing a multi-

plicative effect along the way. Typical PMTs contain 9 to 16 dynode stages. The final step is the collection of the secondary electrons from the last dynode by the anode. As many as 10^6 secondary electrons may be collected as the result of a single photon striking the photocathode of a nine-dynode PMT. The electrical current measured at the anode is then used as a relative measure of the intensity of the radiation reaching the PMT.

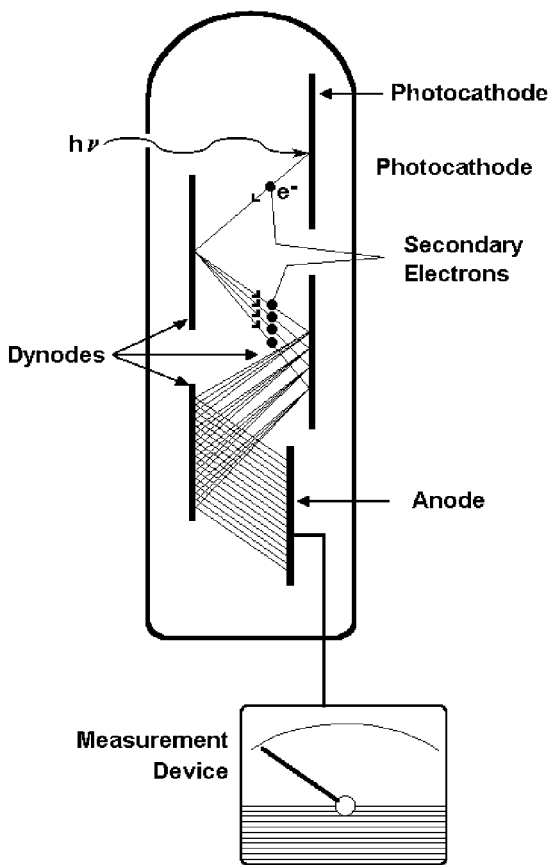


Figure 3-23. Photocathode, dynode and anode layout of a photomultiplier tube.

Figure 3-23 shows schematically how a PMT amplifies the signal produced by a photon striking a photocathode. The major advantages of the PMT over other detection devices are that it can be used to measure light over a relatively wide wavelength range, it can amplify very weak emission levels, and its range of response can be extended to over nine orders of magnitude in light intensity.

Echelle Grating-Based ICP Instrumentation

Wavelength Dispersive Devices. In addition to the classical dispersing device, the diffraction grating, there is another optical component, the prism, which disperses polychromatic radiation into its characteristic wavelengths. In fact, the instrument used by Kirchhoff and Bunsen in the early 1860's to detect the four new elements, Cs, Rb, Tl, and In, incorporated a prism to disperse the polychromatic radiation from the Bunsen flame into monochromatic radiation.

In recent years, it has been shown that certain advantages may be obtained by combining the characteristics of two dispersing systems such as a diffraction grating and a prism or two diffraction gratings. The two optical components are positioned

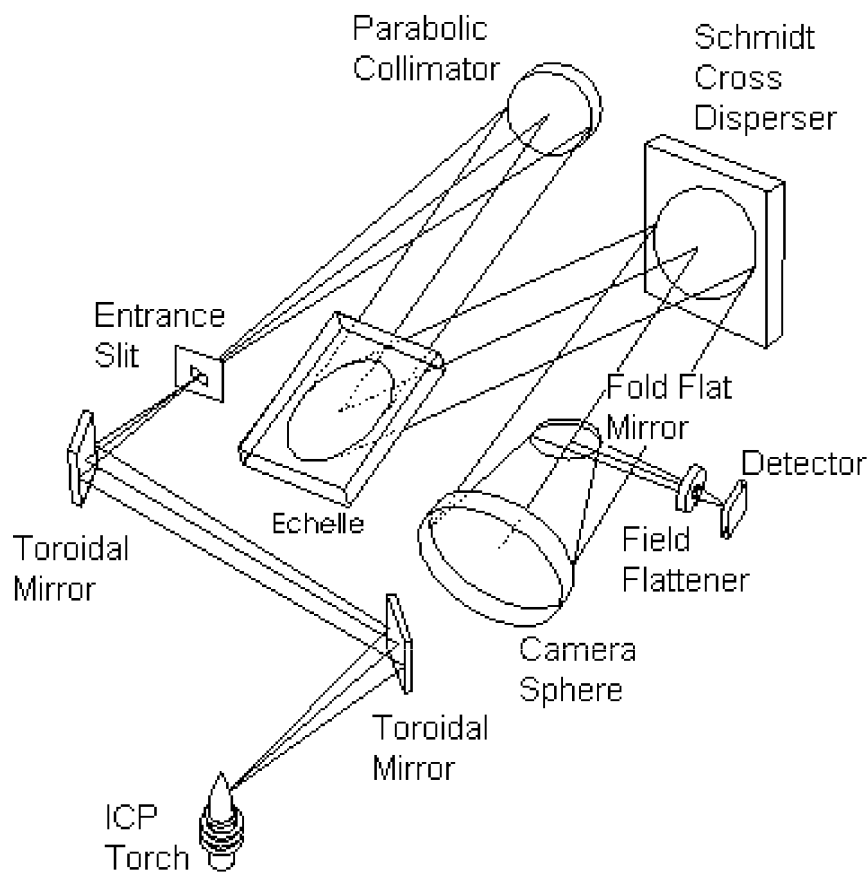


Figure 3-24. An echelle optical mount.

perpendicular to each other. One of the dispersing devices is, in general, an echelle grating which is a very coarse grating in comparison to the normal diffraction grating as described on Page 3-18. The echelle grating separates the polychromatic radiation by wavelengths and produces multiple, overlapping spectral orders. The second dispersing device, either a grating with a ruling density greater than 350 gr/mm or a prism, separates or *cross disperses* the overlapping orders into a two dimensional pattern called an echellogram. A typical optical configuration for this echelle type of spectrometer is illustrated in Figure 3-24. A two dimensional display results at the exit plane—wavelength in one direction and spectral order in the other as shown in Figure 3-25.

Echelle grating-based spectrometers offer some distinct advantages over the conventional spectrometers described on page 3-18. Firstly, the optics result in very good efficiency in each of the spectral orders. Conventional diffraction gratings are generally optimized at a particular wavelength, called the blaze wavelength, and for a particularly order which is usually the first order. Secondly, the system has excellent resolution since it is generally used in the higher spectral orders. (Resolution enhancements are exhibited with increasing order.) Because of the use of higher orders with better resolution, the physical size of the instrument may be reduced thus producing a small instrument footprint.

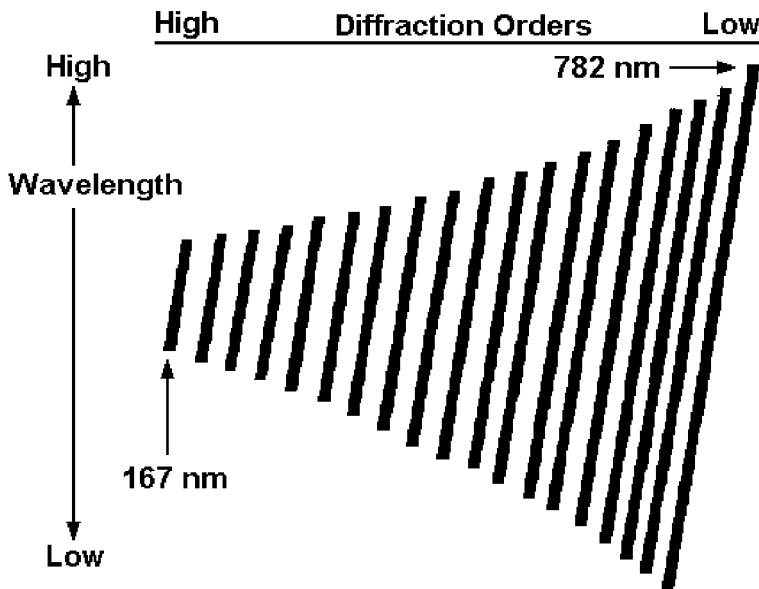


Figure 3-25. Exit plane illustrating the two-dimensional array produced by the echelle mount.

The two-dimensional echelle pattern resulting from the optical design of the echelle spectrometer may be either expanded to fill a rather large surface area or reduced to a small area. For the expanded version, there is sufficient two-dimensional surface area for conventional PMT detection as described on page 3-22 to be used. On the other hand, the smaller area lends itself well to the use of advanced array detection devices.

Advanced Array Detectors

In the 1960s, solid-state devices were introduced into the electronics industry. These devices, such as transistors and diodes, were based on the properties of silicon but were relegated to research and aerospace applications that could afford the relatively high cost of these components. As their use expanded to the digital electronics industry in the form of integrated circuits (ICs), not only did the cost of the devices become affordable but the cost of systems using the ICs such as digital computers were drastically reduced. Today, a small personal calculator can be purchased for less than ten dollars.

It was also discovered that silicon-based sensors responded to light and were quickly integrated into linear and two-dimensional arrays called solid-state imagers or detectors. The commercial need for an affordable television camera drove the market into reducing the cost of the technology. However, since the television camera did not require the sensitivity and resolution that many scientific applications demand, there was a need for higher-quality solid-state detectors.

Consequently, three generic, advanced solid-state detectors with high sensitivity and resolution for spectroscopic applications have been developed - the photodiode array (PDA), the charge-injection device (CID) and the charge-coupled device (CCD). The CID and CCD devices are based on the light-sensitive properties of solid-state silicon and belong to the broad class of silicon-based devices called charge transfer devices (CTD).

To illustrate the principals associated with CTDs, a block of very high purity crystalline silicon is considered (Figure 3-26). Onto this silicon substrate is grown an insulating layer of silicon dioxide (SiO_2). As shown in the pictorial Figure 3-27, each silicon atom in the substrate is bonded to its adjacent silicon atom in a three dimensional lattice. The silicon-silicon bond may be broken by energy of sufficient strength such as photons with visible or ultraviolet wavelength. When the bond is broken, an electron is released within the lattice structure and a subsequent hole in the crystalline structure is formed. This is called an electron-hole pair.

If a voltage is applied across the block of silicon (Figures 3-26 and 3-27), the freed electrons will move in the opposite direction of the applied electric field or toward

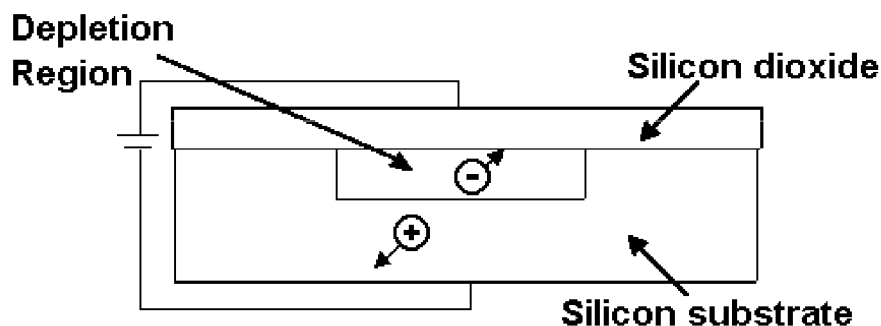


Figure 3-26. Metal Oxide - Silicon (MOS) capacitor.

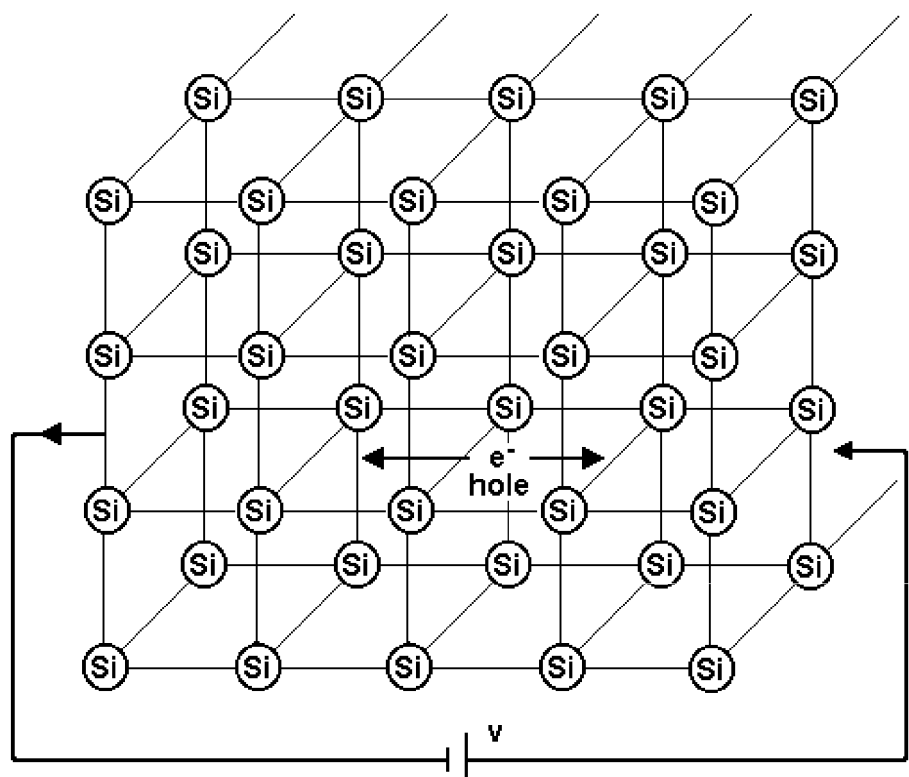


Figure 3-27. Photon absorption by silicon crystalline lattice and the formation of electron-hole pairs.

the silicon-silicon dioxide interface while the holes will move in the other direction or in the same direction as the electric field and leave a region depleted of positive charge. This electron and hole motion within the crystalline lattice creates a current which is proportional to the amount of photons impinging on the structure. That is, the more light absorbed by the silicon, the more electrons are captured at the silicon-silicon oxide interface.

The CTDs elements, called *pixels*, may vary in size from 6 to 30 microns and arranged generally in a two-dimensional silicon wafer configuration from 512 x 512 to 4096 x 4096 pixels. Each of these pixels is capable of storing photon-generated charge. It is the manner in which the charge is obtained, interrogated and stored that distinguish the various types of devices.

In general, each pixel of the two-dimensional Charge Injection Devices (CIDs) may be randomly interrogated to determine the amount of charge that has been accumulated during a measured time to which the device has been exposed to light (called the integration time). With the advent of high speed microprocessors, individual pixels may be examined even during the integration time to determine the accumulated charge. This process of examining the contents does not destroy the contents and, hence, is known as a non-destructive read-out mode. However, even though the CID has a random access and non-destructive read-out, it has an inherently higher noise level or dark current than, for example, a CCD, and requires cooling to liquid nitrogen temperatures to effectively decrease this noise. The dark current of any device is the electronic current that flows in a detector when operating voltages are applied but no light is present.

An ICP spectrometer with a CID detector is commercially available. It utilizes an echelle design and a CID detector with over 250,000 pixels capable of detecting ICP spectral lines across a large wavelength region. The technique produces a "snap shot" of all detectable lines very similar to that observed on a photographic plate in optical emission spectroscopy. Such analytical improvements as background corrections and spectral interference corrections may be accomplished in a post processing mode rather than at the time of analysis.

The charge accumulated on the pixels of a Charge Coupled Device (CCD) must be read sequentially and, in the process of reading the charge, it is destroyed. Hence, the CCD is known to have a sequential, destructive read-out system. The manner in which the CCD read-out system operates has been compared to "tiny" buckets corresponding to the individual pixels of the CCD. The buckets collect the electrons which have been triggered by the photons impinging on the silicon substrate. At the end of the exposure, the pixels are commanded to "empty their buckets". The electrons in the buckets are emptied one row at a time into bucket holders so that, at the read-out electronics, there is a single line of buckets that are tagged with their

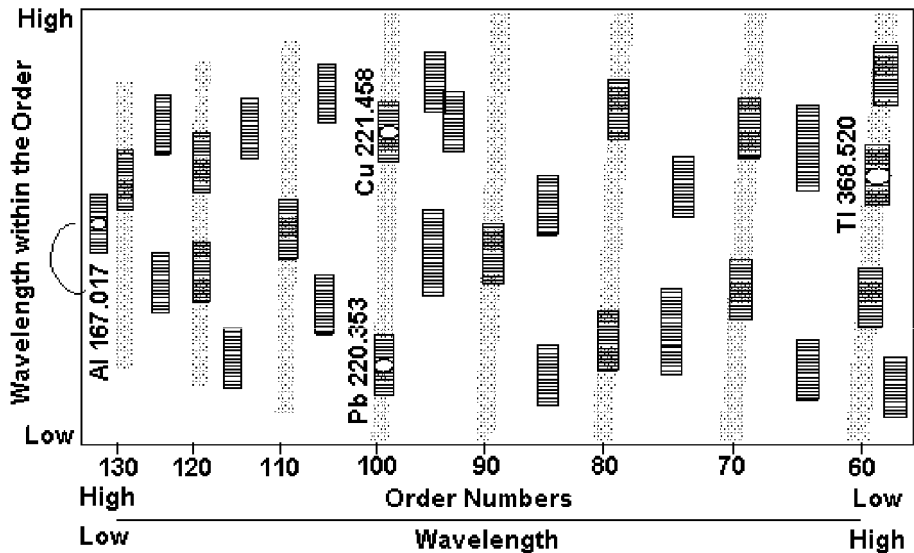


Figure 3-28. Segmented array charge-coupled device detector (SCD)

position in the original array and the content of each bucket is measured. It is easily understood that this bucket brigade operation is a sequential, destructive process whereby the content of an individual pixel cannot be re-examined after the read-out process begins. However, the CCD read-out is extremely fast and has very low noise or dark current associated with the process. Thus, it is possible to cool CCDs by thermoelectric devices such as Peltier units. Furthermore, since most commercial television cameras are CCDs, there is considerable continuing research and development devoted to these types of devices.

Recently, a new type of CCD detector has been introduced—a Segmented-array Charged-Coupled device Detector (SCD) as illustrated in Figure 3-28 - for an echelle ICP instrument. Instead of using a massive CCD with hundreds of thousands of contiguous pixels, the SCD has been designed with individual collection of small subarrays of 20 to 80 pixels each. Each pixel is $12.5\ \mu\text{m}$ wide and 80 to $170\ \mu\text{m}$ in height, the height depends on the wavelength and the echelle spectral order of the spectral line. There are over 200 of these subarrays positioned on a small silicon wafer in a two dimensional pattern associated with the produced echellogram of the echelle spectrometer. These subarrays correspond to the 236 or more of the most important ICP spectral lines of the 70 elements observed in ICP spectrometry.

In Figure 3-29, the details of one of the over 200 subarrays contained on the SCD detector are illustrated. The subarray consists of three areas - the photosensitive

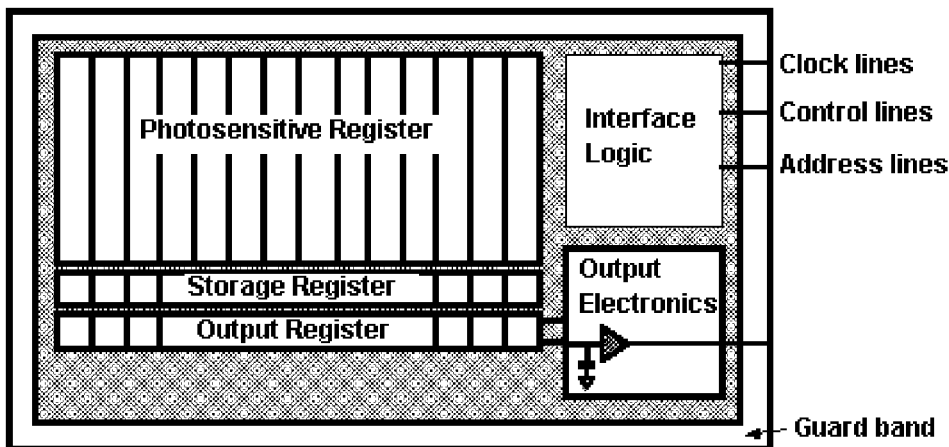


Figure 3-29. SCD Detector Subarray

area, the storage area and the output electronics. Each subarray has its own interface logic which permits individual subarrays to be addressed and read-out. In contrast to most CCDs, the information stored on the small SCD subarrays may be rapidly interrogated in any sequence. Furthermore, most commercial CIDs and CCDs have poor sensitivity below 350 nm because of photon absorption by electrodes embedded on the surface of the device. Because the pixels of the individual subarrays of the SCD have no embedded electrodes, the SCD has good response to light from 160 to 782 nm.

Axial or End-on Viewing ICP Instrumentation

As indicated in Chapter 2, there are several techniques in addition to ICP-OES that are used for trace elemental analysis including FAAS, GFAAS and ICP-MS. Each of these techniques generally addresses a demand in the laboratory for 1) low limits of detection or 2) high sample throughput or 3) a combination of both. Furthermore, depending on the complexity of the matrix, there are distinct advantages for a particular technique. For environmental samples, government regulations and protocols require that only certain techniques be used for particular elements because of detection limits. For example, either GFAAS or ICP-MS instrumentation was required for the determination of As, Se, Tl and Pb because the U.S. EPA's Contract Required Detection Limits (CRDLs) for certain U.S. EPA methods are lower than those obtainable using conventional ICPs. For large sample loads using GFAAS, which measures elemental concentrations sequentially, the analysis times may be quite long. (Recently, sample throughput times, compared to conventional

GFAAS techniques, have improved significantly with the advent of simultaneous atomic absorption (SIMAA) instrumentation in which up to six elements may now be determined simultaneously by graphite furnace techniques.) But, because SIMAAs are limited to a certain number of elements, there have been continuing investigations to find ways to improve the detection limits for ICPs without or in-addition-to the use of hydride generation or ultrasonic nebulization.

As early as 1976, Lichte and Koirtzmann [8] reported that an axially viewed plasma or "end-on" plasma provided better detection limits than the standard radial or "side-on" plasma. By viewing the plasma in the axial direction (Figure 3-19), a longer path length is realized which produces higher analyte emission, improved sensitivity and a 5- to 10-fold improvement in detection limits. However, along with this enhancement, there are increased spectral interference problems and matrix-induced interferences. And because the observations occur through the much cooler tail plume of the plasma, self-absorption effects are quite prevalent which results in reduced linear dynamic range of the source. A few years later, these observations were verified by the investigations of Demers [9] but, in addition, he demonstrated that the matrix-induced interferences could be significantly reduced by use of a shear gas.

Because of the spectral and matrix-induced interferences as well as reduced linear range, commercial axial ICPs did not become available for over 15 years after the original investigations. Even then the initial units were specifically tailored for the GFAAS elements—As, Se, Tl and Pb—and special, background correction procedures were required to obtain, for example, Pb detection limits below the U.S. EPA's CRDLs.

As discussed in Chapter 4, the signals needed for most background corrections are not measured at the same time as the analyte intensity. The analyte intensity is obtained first and then a spectrometer component such as the grating or a refractor plate is moved in order to obtain a wavelength displacement at the exit slits corresponding to the background correction wavelengths. It has been shown that by measuring the background signals at the same time as the analyte line, called simultaneous background correction, detection limits may be enhanced for certain elements. This simultaneous collection of background and analyte intensities removes a source of noise, due to the sample introduction system, from the overall measurement. Furthermore, the simultaneous measurements are faster since no additional analysis time is required to do background correction.

For polychromator systems using PMT detection, simultaneous background corrections may be obtained by simultaneously measuring the analyte intensity in the first order and the background intensity in the second order. On the other hand, advanced, array-based detector systems that obtain a "snapshot" of the ana-

lyte/background wavelength region always realize a simultaneous background correction.

The other problem associated with axial ICPs is the effect of the tail plume on the analytical results. As shown in Figure 3-30, most of the cooler tail plume, where self-absorption occurs, can be displaced out of the optical path by a shear gas. However, even with the displacement of the tail plume, the axial plasma views down the central channel of the plasma and collects all the analyte emission over the entire length of the remaining plasma after the shear gas. This region is much larger than that viewed by a normal radial or normal side-on ICP. In fact, the reason that axial plasmas may exhibit better detection limits than radial ICPs is because the observed region is larger. Along with the increased analyte signal, however, is a decrease in background levels and an increase in spectral interferences. It has been shown that signal-to-background levels may be maximized by optimization of certain physical parameters such as injector tube diameters of the torch and the geometry of the viewed image. As reviewed in Chapter 4, spectral interferences may be either corrected for or minimized by improving resolution, selecting an alternate spectral line with less interference, and/or by applying an interference correction called an interelement correction (IEC) factor. In addition, the original axial ICP instruments did not use a shear gas, thus, limiting the application to fairly "clean" matrices such

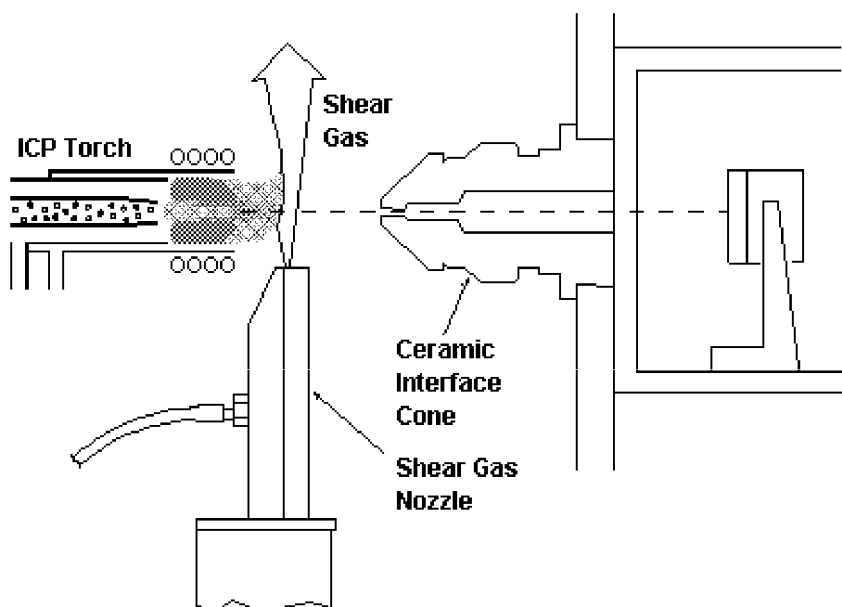


Figure 3-30. Axial (end-on) ICP with shear gas.

as drinking water. With an improved understanding of the mechanics of axial plasmas and the use of a shear gas to effectively remove the tail plume of the plasma from the optical path, axial plasmas have now been shown to be advantageous for many elements in many diverse matrices.

There are several other benefits resulting from the use of axial ICPs. For example, laboratory productivity is greatly improved because sample preparation is reduced, data reduction is simplified and operator training is minimized. Often a separate sample preparation is required for ICP-OES and for GFAAS. With an axial ICP, a single sample preparation is all that is required. This considerably improves the total analysis time, minimizes acid usage and reduces waste generation. Also, since all the results are acquired on a single instrument, report generation is simplified. By performing all the elemental analyses on a single instrument, training is minimized and productivity is increased.

However, because of complex matrix problems and the wide range of elemental concentrations in some real world samples, there may be many cases where axial ICPs are inappropriate for the analysis. A recent commercial development combines the axial and radial configurations into a single unit as shown in Figure 3-31. With this system, the user has the ability to optimize the appropriate configuration for the type of sample without the expense of two separate ICPs.

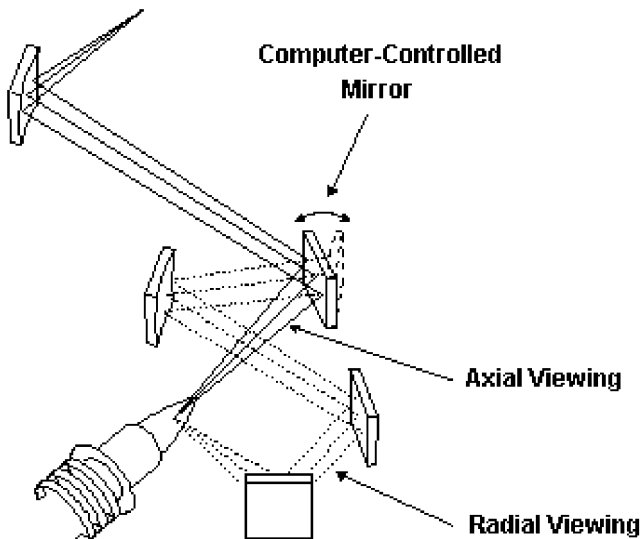


Figure 3-31. A combination radial (side-on) and axial (end-on) ICP.

SIGNAL PROCESSING AND INSTRUMENT CONTROL

Signal Processing

The electronics used for signal processing in ICP-OES systems utilizing PMT detection are generally straightforward. Here, the electrical current measured at the anode of the PMT is converted into information that can be used by a computer or the analyst. The first step is to convert the anode current, which represents emission intensity, into a voltage signal. Since virtually all commercial ICP-OES instruments today, including advanced detector systems, utilize digital signal processing, the voltage signal is converted into digital information via an analog-to-digital, or A/D, converter. This digital information can then be used by a computer for further processing, the end result being information passed on to the host computer or to the analyst in the form of a number representing either relative emission intensity or concentration.

With PMT-base sequential ICPs, it is possible to reprocess stored spectral information, such as background intensities and intensities of spectral interferences, but this data cannot be easily reviewed and changes made at a later date without severe time penalties. On the hand, with advanced detectors, *e.g.*, CIDs and CCDs, a "snapshot" of a wavelength region is obtained and all of the intensities within this region are converted into digital information and may be permanently stored. Thus, post processing of the data is easily accomplished. This means that if it is found 1) that the data might be susceptible to some spectral interference that was not previously corrected for or 2) that the background correction was performed at the wrong wavelength, then these corrections can still be applied and the analyte concentrations recalculated.

Computers and Processors

An important part of any ICP-OES instrument is the computer control incorporated into the instrument. The majority of automated functions of an ICP-OES instrument are directly controlled by an on-board computer. For the simplest instruments, the analyst interacts directly with the on-board computer through buttons or a keypad located on the instrument. All ICP-OES instruments, however, use an external computer, interfaced to the instrument's on-board computer, to act as an interface between the analyst and the instrument.

At the simplest level of multielement ICP-OES instrumentation, a computer is needed to handle the massive amounts of data that such an instrument generates. While virtually every commercial ICP-OES instrument available today uses some type of computer to control the spectrometer and to collect, manipulate, and report analytical data, the amount of computer control over other functions of the instru-

ment varies widely from model to model. For many instruments, the generator controls, argon flows, viewing height, and other variable parameters are controlled manually by the user. In the most sophisticated ICP-OES instruments, every function of the instrument is automated, *i.e.*, under the control of the computer.

In addition to the obvious benefits of using computers for data collection and reporting, automation in ICP-OES instrumentation has other important advantages. For example, when the plasma is ignited, adjustments to the input power, the matching circuitry, and the gas flows may need to be made. In the early days of ICP-OES, these adjustments were made manually, making the utility of the ICP instrument partially dependent on the manual dexterity of the operator. Manual adjustments of the RF generator and argon flows upon ignition have now been made obsolete by automatic matching networks and computerized flow controls. Additional automated functions, such as automatic control of sample selection, nebulizer washout, and operating parameters, have vastly improved the speed and quality of the analytical determinations.

Software

At least as important as the degree of automation of an ICP-OES instrument is the computer software that controls the instrument and through which the analyst communicates with the instrument. While the issue of computer software may be a highly subjective topic for many analysts, there are certain aspects of software that warrant discussion in this chapter on instrumentation.

There have been many philosophical discussions regarding the attributes of the ideal analytical instrument. Some of the attributes of the "ideal" ICP-OES instrument would be that it could prepare the standards and samples, develop the analytical method, analyze the samples, report the results, and make decisions based on those results - all from a single keystroke. The expertise and hardware required to perform all of these tasks is readily available today. However, it is the software required to coordinate these tasks which is presently unavailable.

While the "ideal instrument" software is not yet a reality, the role of software in the operation of an ICP-OES instrument is still important. The objective of a good software package is not only to control the automated features of the instrument during collection of analytical data but to simplify the overall operation of the instrument. Areas in which this is important include not only running an analysis but developing analytical methods and reporting results. The methods development task involves selecting proper operating parameters for an analysis, such as wavelengths, PMT voltages, background correction points, and standards concentrations. The ability to view spectral data displayed graphically with a minimum of effort is indispensable during the selection of these parameters.

In the section "Other Spectral Interference Corrections" of Chapter 4, a description of another important tool for the analyst is presented - Multicomponent Spectral Fitting (MSF). MSF is a processing mode that distinguishes analyte spectra from interfering spectra by the use of stored mathematical models. This could not have been incorporated into ICP instrumentation without significant advancements in computer technology and related software.

The use of "chemometrics" in ICP-OES software has become more prevalent in recent years. chemometrics-based software features can automatically select parameters such as background correction points [12], and perform intelligent optimization studies without user interaction [10,11]. The development of the ideal instrument software in the future is going to be dependent somewhat on advances in user interface design and algorithm development.

ACCESSORIES FOR ICP-OES INSTRUMENTS

Autosamplers

The most widely used accessory for ICP-OES instruments is the autosampler. Typical autosamplers have a capacity of almost 100 samples while some larger models can hold 300 - 500 samples. The main function of the autosampler is to free the analyst from having to switch the sample input tubing manually from one solution to the next. Ideally, the analyst should be able to load the autosampler with standards and samples, start the analysis, walk away from the instrument, and return to find the analysis completed. This is called *unattended* operation and has particular relevance to laboratories with high sample throughput requirements.

A recent development is an autosampler designed to handle small volume samples (~1 mL volume or less). Sample types which may be volume-limited include biological, clinical, semiconductor, and radioactive samples. The small size of this particular autosampler allows easy placement in a glove box for handling very clean samples or biohazards.

Sample Introduction Accessories

Also widely used with ICP-OES instruments are a variety of sample introduction accessories such as ultrasonic nebulizers, direction injection nebulizers, hydride generators, graphite furnaces, and spark and laser ablation systems. Some of these devices, described at the beginning of the chapter, are available directly from ICP manufacturers while others must be purchased separately.

Even though, in general, there are five orders of magnitude of calibration curve linearity for ICPs, which is sufficient for trace elements in most applications, there

may be certain samples where the analyst wishes to determine both trace and major constituents. Consequently, there is a need in ICP-OES for autodiluters, usually working in concert with an autosampler, not only for sample dilution but also for standard preparation and reagent addition. These devices would allow 10- to 1000-fold dilutions to be made automatically and under computer control.

Organic solvents are often difficult to analyze by ICP-OES because of their high volatility. Problems include plasma instability and elevated carbon emission backgrounds both of which compromise detection limits. If a second desolvation unit is placed after the normal desolvation system on the ultrasonic nebulizer, illustrated in Figure 3-8, further reduction in solvent loading is realized. This secondary desolvator consists of a porous Teflon membrane mounted in a small oven. Solvent vapor will pass through the pores of the membrane while analyte particles continue to the ICP. Much less solvent vapor reaches the ICP so the problems listed above are mitigated and organic solvent detection limits are improved.

Liquid chromatography may be interfaced to ICP-OES for on-line detection of separated components of a sample. A series of microcolumns are available for separations involving small volume samples. Of particular interest is the need for elemental speciation: the separation and detection of different forms of an element. For example, the determination of total chromium in a sample may not reveal the true nature of the sample since Cr^{+3} is relatively harmless while CrO_4^{2-} is very toxic.

4 ICP-OES METHODOLOGY

The analysis of samples by ICP-OES is generally a simple task. This simplicity is due in large part to the versatility of the ICP-OES technique and the relative lack of interferences encountered. In addition, the use of computers and automated features on ICP-OES instruments has simplified or even eliminated many of the tasks that were previously required for ICP-OES analyses.

Even though significant advances have been made since the introduction of the ICP-OES technique, there is still a certain amount of interaction between the analyst and the instrument that is required for ICP-OES analyses. The skill required of the analyst can vary widely depending on the types of samples to be analyzed and the sophistication of the instrumentation used. With some state of the art ICP-OES instruments and for some sample types, the only decision the analyst needs to make is which elements are to be determined in the sample. Predetermined or default parameters will then be used in the analysis. On the other hand, much more skill and time may be required to analyze a sample about which little is known. Decisions may need to be made regarding sample preparation, wavelengths to be used, standard solution concentrations, and potential interferences. Fortunately, the necessary decisions for analyzing the vast majority of samples are relatively easy to make once the criteria for making them are understood. The collection of techniques, parameters and tools used for a particular analysis is known as the *methodology*.

There are several features common to the ICP-OES methodology used in any analysis. Sample preparation, sample introduction, instrument calibration, and element or wavelength selection are part of every ICP-OES analysis. For some analyses, the analyst must also consider interference corrections and optimization of operating parameters. In this chapter, an overview of ICP-OES methodology is given followed by a generalized discussion of interferences encountered in ICP-OES. The bulk of the chapter is then devoted to more detailed discussions of what decisions may be required for each step of the methodology, what pitfalls or interferences are commonly encountered and how these problems are overcome.

This chapter is not meant to be a "how to" guide for the application of the ICP-OES technique to specific analyses. Indeed, the goal of this chapter is to provide an indication of the types of decisions that need to be made to perform an analysis and

the level of expertise needed to make these decisions. The information in this chapter should help the potential ICP user make better-informed decisions regarding what type of ICP-OES instrument to buy or use and what skills are required to set up and perform ICP-OES analyses.

An Overview of ICP-OES Methodology

Figure 4-1 shows a flow chart for the steps in a typical ICP-OES analysis. The first decision required in developing the methodology for an ICP-OES analysis is which elements are to be determined in the sample. Much of the subsequent methodology is based upon this first decision. Other than making sure that the elements can be determined on the user's instrument, the selection of elements is determined by the user's own requirements for trace elemental analyses. Once that decision has been made, the analyst's goal is to determine the best way to carry out the analysis.

The first step in an analysis is to prepare the samples and standards for introduction to the ICP. This step depends on the physical and chemical characteristics of the samples and runs the gamut from simple dilution to a complex series of chemical reactions and other preparation steps. The next step in the analysis concerns the sample introduction method and hardware to be used. For most ICP-OES analyses, the standard sample introduction system provided with the instrument will suffice. An example of when a nonstandard system might be used is when the solutions to be analyzed contain high levels of particulates or dissolved solids.

The next step in the development of an analysis methodology is to program the instrument, using the computer software provided with the instrument, to perform the data collection and processing steps. To do this, decisions must be made concerning the operating conditions, wavelength selection, instrument calibration, emission measurement, and the actual sample analysis. For many analyses, the default conditions recommended by the instrument manufacturer will provide satisfactory results.

Before making analytical measurements using the instrument, the analyst should take the necessary steps to determine that the instrument is set up and functioning properly. Valuable time and effort, not to mention irreplaceable samples, may be wasted by running an analysis on an instrument that is not set up properly. Appendix A contains some information regarding instrument maintenance and performance verification. The analyst may find this information helpful in assuring that an ICP-OES instrument will provide acceptable analytical results.

Once the samples and standards are prepared, the hardware is set up properly, and the computer is programmed, the analysis may begin. The analyst usually starts by introducing the first standard solution to the plasma and pressing a key

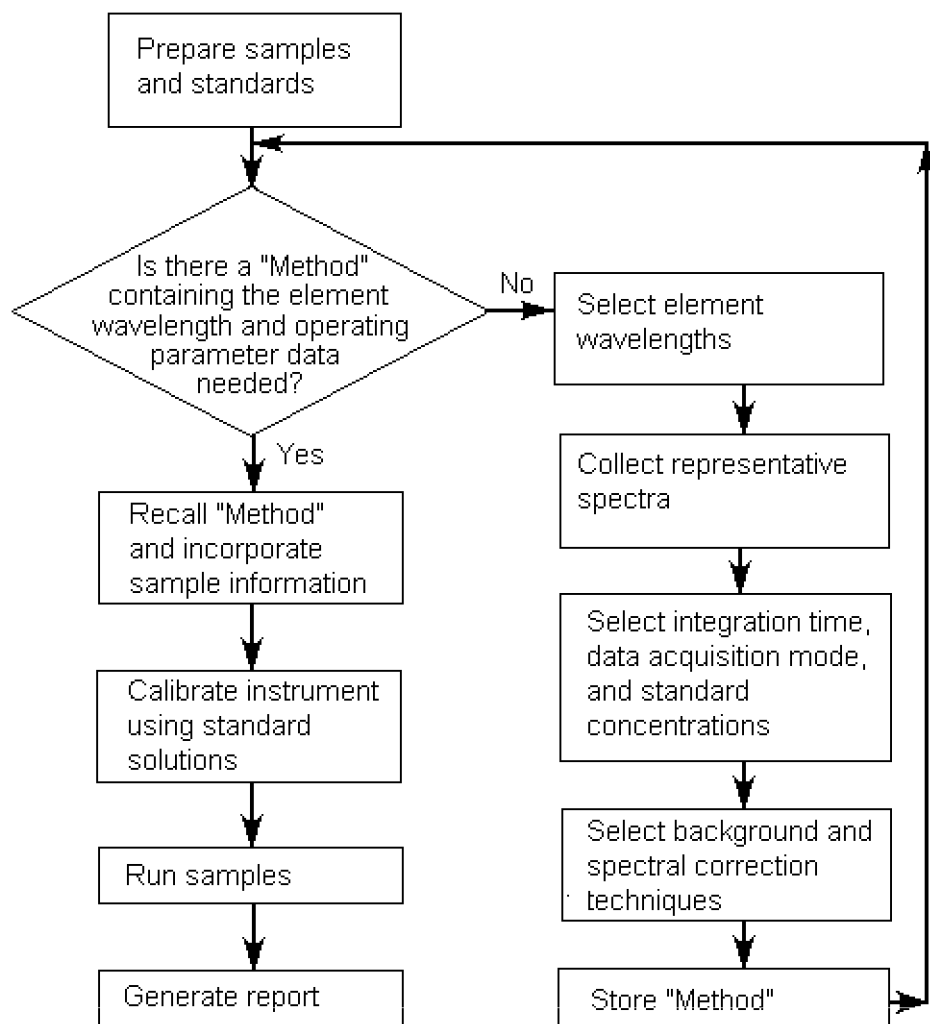


Figure 4-1. Flow chart showing the methodology for a typical ICP-OES analysis.

on the computer. Assuming everything is found to be working properly, the analyst continues by introducing further standards (if used) and a blank solution to complete the calibration of the instrument. If no other calibrations or checks are required, the calibration is followed by introduction of samples. Intertwined throughout the analysis may be various solutions used for quality control purposes. Once the analysis of samples is completed, the results can be tabulated and reported as necessary.

One of the biggest advantages of the general simplicity of ICP-OES methodology is that once a method is developed, the ICP-OES technique lends itself very well to the use of automation. Even for sample preparation, there are a few automated sample preparation systems available. But once analysis begins, relatively little user interaction is generally required. In fact, automation techniques have been developed to the point that the analyst can simply load the unprocessed samples onto a tray, press a few keys on a computer keyboard, walk away from the instrument, and return to find the analysis completed.

ICP-OES Interferences —General Considerations

Before moving on to discussions of the specific steps involved in development of ICP-OES methodology, it is appropriate to discuss interferences in a general sense. To the analytical chemist, an interference is anything that causes the signal from an analyte in a sample to be different from the signal for the same concentration of that analyte in a calibration solution. Despite the fact that the presence of an interference can be devastating to the accuracy of a determination, there is no analytical technique that is completely free from interferences. However, modern trace elemental analysis instruments have been designed to minimize the interferences.

When ICP-OES was first introduced to the analytical community, the claim was often made that the technique was nearly free from interferences. This claim was made because the classic chemical interferences that were found in flame atomic absorption spectrometry were not observed in ICP-OES. Soon after analysts began measuring trace element concentrations in a wide variety of samples, however, the reality of the existence of some interference became apparent. The interferences that we know about today in the ICP are spectral in origin. Other interferences are often the result of high concentrations of certain elements or compounds in the sample matrix and are not too severe for most samples.

The best way to guard against inaccurate results due to unexpected interferences with ICP-OES (or any other technique for that matter) is an adequate quality control program. The components of quality control will vary with the sample type, the degree of precision and accuracy required, and the penalty anticipated if errors exceed acceptable levels. The most generally applicable quality control procedure is to analyze samples of known composition along with the unknowns. These reference materials should match the sample matrix and the concentration range of the analyte elements.

Reference materials representing many different types of matrices with numerous certified trace element concentrations can be purchased from the U. S. National Institute of Standards and Technology (formerly the National Bureau of Standards).

Other government-related sources of reference materials include the U.S. Environmental Protection Agency, the International Atomic Energy Agency, the Bureau of Analysed Samples, Ltd. (U.K.), the Community Bureau of Reference (Belgium), and the National Research Council of Canada. Several commercial manufacturers, such as Spex, Inorganic Ventures, High Purity Standards, MV Labs, PLAS-MACHEM Associates, Solution Plus, and VHG, also offer certified standards. Furthermore, most ICP instrument manufacturers as well as catalog houses including IEM Science, Fisher Scientific, GFS Chemicals, J. T. Baker, and VWR carry ICP-OES standards.

Preparation of Samples and Standards

Preparation of samples for analysis by ICP-OES can be as simple as putting the sample into an autosampler tube or as tedious as to require several days of mixing, dissolving, heating, filtering, and diluting. Because the vast majority of samples analyzed by ICP-OES are introduced as solutions, the discussions in this section are geared toward samples that are already in solution form or can be put into solution. Solid and gaseous samples that are not put into solution before introduction to the ICP generally need little preparation, but rather require special sample introduction methods and hardware.

The basic goals of sample preparation for ICP-OES are to 1) put the sample into solution (if it is not already in solution), 2) stabilize the sample-containing solution especially if low concentrations of analyte are present, 3) make the analyte concentration fall within the working range of the instrument through dilution or preconcentration, and 4) ensure that the sample-containing solution can be nebulized in a reproducible manner. The third goal may be difficult for samples that contain both very high and very low concentrations of analyte species. In these cases, it may be necessary to prepare two different dilutions of the sample.

Solid samples are generally dissolved in acids before introduction into the ICP. This process, called *acid digestion*, quite often requires heating the digestion solution, which contains the sample and acid(s), with a hot plate or a microwave oven. It is not unusual for an acid digestion procedure to take several hours, although the use of microwave ovens specially designed for sample preparation can reduce the digestion time dramatically. Liquid samples that contain particulates may also require a digestion procedure to dissolve the particulates or filtration to remove the particulates if the particulates do not contain significant amounts of analyte. Some solids that are particularly difficult to dissolve may require a *fusion* reaction, in which the sample is reacted with a compound such as lithium metaborate and then dissolved in an appropriate matrix.

Aqueous samples may require dilution with water and are usually stabilized with an acid before analysis by ICP-OES. Organic-based liquid samples may require dilution with an appropriate organic solvent to make the sample easier to nebulize. Other sample preparation techniques include extractions, neutralizing reactions, and preconcentration via evaporation or ion exchange.

The amount of solution needed for an ICP-OES analysis depends on how many elements are being determined, how many replicate measurements are going to be taken, and the speed of the instrument itself. The peristaltic pumps used for ICP-OES usually deliver the standard and sample solutions at the rate of about 1 mL/min. At this rate, if an instrument takes 5 minutes to analyze a sample, then 5 mL of sample solution would be required.

While most ICP-OES sample introduction systems can tolerate high acid concentrations, there are some other possible restrictions on the acids used for ICP-OES sample preparation. For example, phosphoric and sulfuric acids can contribute to background emission observed in the ICP. For analyses where this background emission may cause an interference, nitric and hydrochloric acids are more desirable for preparation of samples. In some cases, the possibility of precipitation of the analyte may dictate the selection of an acid to prepare a sample containing silver as an analyte since the silver could precipitate from the solution as AgCl. In the early days of ICP-OES, it was usually suggested that hydrofluoric acid not be used for digestion procedures since HF can etch the glass and quartz components of the sample introduction system and torch. This limitation has been nearly eliminated by the availability of HF-resistant sample introduction systems and torches for most modern ICP-OES instruments.

Preparation of standards for ICP-OES is done by dissolving high-purity metals or salts with high-purity acids or other appropriate reagents and then diluting to obtain the desired concentrations. Also available from a wide variety of vendors are standard solutions that can be diluted as necessary by the analyst. When preparing *mixed standards*, i.e., standards containing a known concentration of more than one element, one must make sure that the elements of interest are compatible with the other species in the solution so that precipitation of the standard elements does not occur.

An important concept related to sample preparation and interference correction is that of *matrix matching*. Matrix matching involves preparing solutions whose major concerns match those of another solution. While matrix matching certainly involves matching the solvents, it also involves matching the concentrations of acids and other major solutes. For example, if one wanted to matrix match a standard to a steel sample solution containing 10% Fe, he or she would add enough iron to the standard so that the iron concentration of the standard matched that of the sample.

When preparing the blank solution to be used in the standardization process, it is recommended that the blank be matrix matched with the standard solution(s) to be used. For analysis of most common aqueous samples, this would usually involve adding a specified amount of acid to some deionized water.

Other than using the same solvent for the standard and samples, it is usually not necessary to matrix match the standards and samples exactly, except as a last resort for correcting for interferences. However, if it can be done easily, it is suggested that the acid contents of the standards and samples be matched. In cases where the standard and sample matrices are quite different or cannot be matched and an interference occurs as a result, a technique known as *internal standardization* is often used. In this technique, an element, known as the internal standard, is added to the standards, blanks and samples. The analyte compatibility rules which apply to selection of acids and creation of mixed standards also apply when adding internal standards. The internal standardization technique is described in more detail in the next section.

Sample Introduction

In selecting a sample introduction method for ICP-OES, the analyst should generally consider the requirements for sensitivity, stability, speed, sample size, sample type, corrosion resistance, and resistance to clogging. Cost and ease of use may also be considerations. Several sample introduction techniques and the related hardware offerings are described along with their relative advantages and disadvantages in Chapter 3. For most samples, a cross-flow nebulizer combined with a corrosion-resistant spray chamber and torch offers the best compromise for the above requirements.

In certain cases, the differences in the matrices of the standards and the sample are great enough to cause the sample introduction efficiencies for the standards and the sample to differ. Such differences in sample introduction efficiency represent an interference since an equal concentration of analyte in the standard and in the sample would not result in equivalent emission signals. These matrix interferences often originate from differences in surface tension and/or viscosity between the standards and the samples. The matrix interference most commonly encountered in ICP-OES results from high concentration of dissolved solids in the sample solutions.

Special techniques may be required to obtain accurate results when a difficult matrix interference is present. One of the most popular techniques for correction of matrix interferences is internal standardization. In this technique, an element known as the internal standard (or internal reference) is used to indicate the relative amount of sample that is transported to the plasma. The internal standard is an element

that is present at the same concentration in all solutions to be analyzed - standards, blanks, and samples. This element can either be one that is present as part of the matrix for all the solutions or one that is added to the standards, blanks and samples during sample preparation. In this latter case, the internal standard element must not be previously present in the samples at a detectable concentration. The emission signal from the internal standard is then used to correct mathematically for differences in sample introduction efficiencies. Alternatives to internal standardization may include matrix matching the standards, blanks and samples, diluting the samples or using the method of additions.

Operating Conditions

The conditions used for the operation of the ICP and the measurement of emission are important for any ICP methodology. For routine analyses, the standard operating conditions as suggested by the instrument manufacturer are usually sufficient. Virtually every ICP-OES instrument has two sets of standard conditions - one for aqueous solutions and one for organic solutions. Some typical standard operating conditions are given in Table 4-1.

Table 4-1
Example of standard operating conditions for an ICP-OES instrument.

| <u>Operating Parameter</u> | <u>Aqueous</u> | <u>Organic</u> |
|-------------------------------------|----------------|----------------|
| RF Power (kW) | 1.0 | 1.5 |
| Outer argon flow (L/min) | 12.0 | 15.0 |
| Intermediate argon flow (L/min) | 1.0 | 2.0 |
| Inner argon flow (L/min) | 1.0 | 0.7 |
| Nebulizer uptake rate (mL/min) | 1.0 | 0.7 |
| Viewing height (mm above load coil) | 15.0 | 15.0 |

Some analyses, however, may require that the analyst deviate from the standard operating conditions. Determination of analyte concentrations that are near the detection limits, the need for high-precision analyses and the presence of high salt concentrations in the sample are examples of when the analyst may want to use nonstandard operating conditions.

The operating conditions of an ICP-OES instrument are determined by a number of variable parameters. The most common parameters that are varied, depending on the design of the instrument, are integration time, PMT voltage or gain for

classical PMT-type systems, argon flow rates, and RF power. Other variable parameters may include pump speed and viewing height. (Wavelength is certainly an important variable parameter on many instruments. Selection of wavelength is considered in the next section of this chapter.)

In general, the more variable features an instrument has, the more flexible that instrument is. There is, however, a price to pay for this flexibility. Because the cost of an ICP-OES instrument is partly determined by the number of variable features and the degree of automated control of these features, flexibility can vary widely from instrument to instrument and is somewhat reflected in the price of the instrument. Before selecting a particular instrument, the analyst should determine how much flexibility will be required since many ICP-OES analyses do not require a great deal of flexibility.

The parameters that are variable on an ICP instrument are generally those that change the operating conditions enough to influence the outcome of an analysis. Short explanations of the effects resulting from the variation of some of these parameters are given below.

A parameter that may be important in an analysis is integration time, or the time spent measuring the emission intensity at each wavelength. While the precision of an analysis can be improved, within certain limits, by increasing the integration time, there is also a trade-off in the speed of an analysis when a longer integration time is used. For sequential multielement analysis, it may be possible to use a different optimized integration time for each element. In this way, a longer integration time could be used when the emission signal for an element is expected to be weak, while a shorter time may be used for an element with a strong signal. These principles apply not only for systems utilizing PMTs but also for those incorporating advanced detectors.

For PMT-based ICP-OES systems, the PMT voltage setting, or amplifier gain on some instruments, is a function of the expected intensity of the emission to be measured. A high voltage/gain setting is used for measuring weak emission while a lower voltage/gain is used for measuring strong emission lines. Most present ICP-OES instruments have detection electronics that can measure light intensity over five or six orders of magnitude using a single PMT voltage setting, making the selection of PMT voltage less critical than for earlier ICP-OES instruments that had more limited response ranges.

The inner or nebulizer argon flow rate can be a critical parameter because it largely determines the residence time of the analyte species in the center of the plasma discharge. The longer the residence time, the more time the analyte has to be atomized, excited and ionized. For an element that emits strong ionic lines and also

has a high ionization potential (*i.e.*, requires more energy to ionize), a long residence time would be desired. Thus a lower inner argon flow rate might be used to obtain maximum sensitivity for this element, as long as the nebulizer efficiency does not fall off significantly when the nebulizer flow is changed. At this lower flow rate, the analyte would travel through the plasma at a slower speed, giving the analyte more time within the hot region of the plasma to be ionized and excited. On the other hand, for elements such as sodium and potassium that emit strong atomic lines and are easily ionized, a faster flow rate might be used so that the atoms are not ionized before they can emit the desired radiation.

Similar to nebulizer flow rate, the RF power applied to the plasma can be optimized according to the nature of the analyte species. The more power that is applied to the plasma, the hotter the plasma gets. For analyte species that require more energy for excitation and ionization, a higher power would provide greater sensitivity. For an easily excited analyte, such as the sodium example mentioned above, a lower power would increase sensitivity.

Especially for radial or side-on ICPs, viewing height is another parameter that can be optimized for a particular analyte species. The viewing height, usually measured as the distance above the top of the load coil, is used to indicate the region of the plasma discharge being observed by the spectrometer. Figure 2-3 in Chapter 2 showed the various regions of the ICP discharge as characterized by their temperatures. The combination of varied temperatures and residence time effects makes some regions of the ICP better for certain types of emission than other regions. Figure 4-2 shows how the yttrium atomic emission and ionic emission originate from distinctly different regions of the plasma. Depending on which elements are being determined, the analyst may choose to vary the viewing height for the analysis. Because varying the RF power and/or nebulizer argon flow can often be used to accomplish the same analytical goal as varying the viewing height, some lower cost ICP-OES instruments may not offer adjustable viewing height.

For the applications that require the use of optimized conditions to obtain sufficient sensitivity and precision, it is important that the ICP instrument to be used features automatic (computer) control of the parameters that need to be varied during the analysis. If the control of the variable parameters is manual, then each of the elements must be determined individually, or in groups having similar optimum parameters, so that the analyst can set up the instrument for each set of operating conditions. Certainly, this could lengthen the analysis time considerably and would most likely preclude efficient use of an autosampler for the analysis.

Besides using non-standard operating conditions for certain elements, non-standard conditions are also used for certain sample types. Note that in Table 4-1 the standard argon flow rates and RF power are different for organics than for aqueous

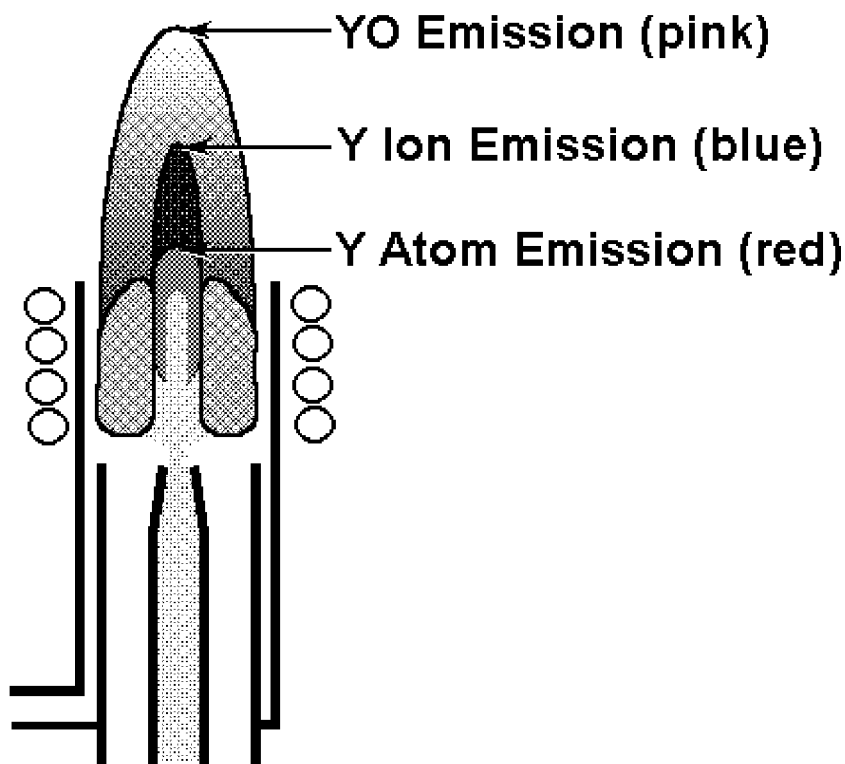


Figure 4-2. Yttrium atom, ion and oxide emission from an ICP discharge.

samples. These differences in operating conditions are dictated by the sample matrix rather than the elements to be determined in the samples. Some sample matrices require analysis at increased power levels simply to sustain the plasma during the analysis. While the conditions listed in Table 4-1 are sufficient for most aqueous and organic samples, there are some possible interferences, described below, that may require further optimization of various parameters.

The majority of the interferences observed in flame atomic absorption spectrometry are chemical (vaporization) interferences. Chemical interferences arise when some element or molecule in the sample causes a particular analyte element to vaporize either more or less quickly than the analyte vaporizes in a solution without the interferent. A classic example of a chemical interference is the effect of aluminum on calcium. When a sample contains both aluminum and calcium, the calcium absorbance signal can be reduced by up to 80% in a flame. However, since the ICP discharge is much hotter than the flames used in atomic spectrometry, sample

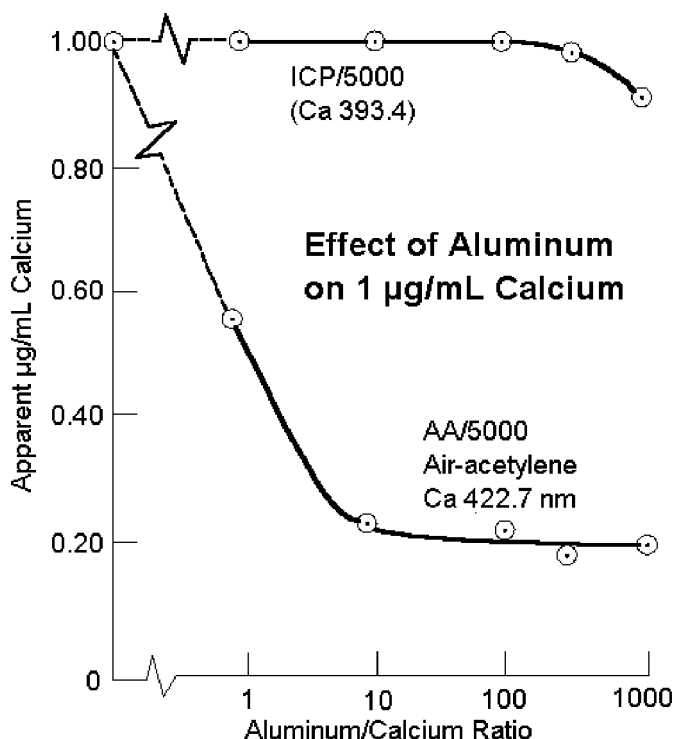


Figure 4-3. Comparison of the effect of aluminum on the determination of calcium by flame AAS and ICP-OES.

vaporization is more complete and the effect of aluminum on the calcium emission signal is not nearly so severe. Figure 4-3 shows the relative effects of increasing aluminum concentration on the apparent calcium concentrations determined by flame AAS and ICP-OES. In most cases, chemical interferences are not observed in ICP-OES. In the few extreme cases where this interference does exist, it may be necessary to increase the RF power and/or reduce the inner argon flow to eliminate a chemical interference.

An example of another type of interference occasionally encountered in ICP-OES is the so-called "easily ionized element", or EIE, effect. The EIEs are those elements that are ionized much more easily (*i.e.*, at lower temperatures) than the other elements in the periodic table. Examples of EIEs are lithium, sodium, and potassium. In samples that contain high concentrations (greater than 1000 ppm) of EIEs, suppression or enhancement of emission signals, depending on the analyte species, is possible. Recent studies [13] have shown that not only the EIE elements,

but other elements such as calcium and iron may also cause similar interferences when present at high concentrations.

In the early days of ICP-OES, samples containing high concentrations of EIE-containing salts (for example, more than 0.5% NaCl) were usually diluted before analysis because the high dissolved salt concentration would cause clogging of the nebulizer. Because the concentration of the EIE was thus reduced, compensation for EIE effects was generally not necessary. Some of today's nebulizers, however, are capable of nebulizing solutions containing over 20% NaCl and similar salts. The analysis of such samples may require the use of non-standard operating conditions, such as using a higher RF power setting, to compensate for the EIE effect and other matrix-induced interferences. For cases in which an extreme interference exists, it may also be necessary to apply mathematical correction techniques to compensate for the interference [13, 14].

Wavelength Selection

The selection of wavelengths for measurement of the emission from the analyte elements is done using several criteria. First of all, the wavelengths must be accessible with the instrument being used. In the case of classical PMT-based polychromator ICP-OES instruments, the wavelength selection may be compromised because of space restrictions, *i.e.*, the juxtaposition of exit slits and PMTs, within the spectrometer. For instruments whose spectrometers do not have vacuum and/or purging capabilities, wavelengths below 190 nm cannot be used.

The second criterion for selection of wavelengths is that the wavelengths selected be appropriate for the concentrations of the elements to be determined. When the analyte concentration falls outside the working range of an emission line, a different emission line should be used. For example, if the manganese concentration in a sample is expected to be about 200 mg/L, then the most sensitive emission line, at 257.610 nm, should not be used since the upper end of its working range is about 50 mg/L. In this case, a less sensitive line, such as the line at 294.920 nm, would be more appropriate. Of course, when working at or near the detection limit for an element, the most sensitive line is usually the best choice. With advanced detector systems, such as the CID or SCD ICP-OES instrumentation, these highly sensitive and less sensitive lines are available for all ICP determinable elements.

Another criterion may be the nature of the origin of the emission lines, *i.e.*, ion transitions vs. atom transitions. For example, a certain type of line may be less vulnerable to interferences such as the EIE effect and thus may be preferred in some applications. In analyses where internal standardization is used, it may be preferable to match analyte ion lines with an internal standard ion line and analyte neutral atom lines with an internal standard neutral atom line.

The final criterion is that the wavelengths be free from spectral interferences. Because the ICP is so proficient at causing almost any element to emit numerous emission lines, this criterion is sometimes difficult to meet. When freedom from spectral interferences is not possible, lines whose emission intensities can be corrected for spectral interferences should be used. Because correction of spectral interferences is such an important part of ICP-OES methodology, a separate section containing details about spectral interferences and methods for correction of them is included at the end of this chapter.

Emission Measurement

The method used for the measurement of emission is usually built into the instrument itself and cannot be easily modified by the user. Knowing how the instrument measures emission can be important and may help the analyst to avoid certain problems that may be encountered. The most common two ways to measure emission are to scan the spectrometer over a small wavelength region surrounding the expected emission lines, making a measurement at each step, or to set the spectrometer to a specific wavelength and make measurements only at that wavelength. Some ICP-OES instruments use a combination of the two methods. Today, there is a third way which is offered by Echelle-based, CID or SCD advanced detector systems. These instruments measure and record simultaneously the emission of most spectral lines and their associated backgrounds emitted by an ICP. It has been compared to obtaining a "snapshot" of either the entire wavelength region of interest or specific regions surrounding the most important emission lines.

The main advantage of the first method, known as the "peak search" or "wavelength optimization" method, is that the analyst is assured that measurements are taken at the peak of the emission line. This is especially important in sequential ICP-OES instruments because of their scanning mechanics. For certain background correction methods, the use of the peak search methods are also advantageous.

Advantages to "sitting on a peak", as the second method is often referred to, are: 1) the time saved by not having to slew to the wavelength, 2) the time saved by not having to scan over the peak, and 3) it makes use of spectral interference correction techniques, known as interelement corrections (IECs), more straightforward. However, when using the "sitting on a peak" method, the user must be careful to assure that the instrument is in proper wavelength alignment. In fact, if wavelength drift has occurred, the spectrometer may not be set to the correct wavelength and may be measuring the side of a peak instead of the peak maximum which would result in poor accuracy even though the precision may be acceptable. This "sitting on a peak" method of emission measurement is used with practically all simultaneous ICP instruments including the new advanced detector systems and with a few sequential instruments.

With advanced detector methodology, hundreds of ICP-OES emission wavelengths with their associated background are obtained simultaneously. Not only does this permit background correction and spectral interference corrections to be easily applied, the corrections may be made at a later time than the actual analyses which is called *post-processing* of the data. Because all the spectral information is stored, it is even possible to apply the use of internal standardization at some future time if the internal standard lines were included in the method.

While the method of emission measurement is usually fixed for a given instrument, there are certain parameters associated with the emission measurement that can usually be modified to fit the analyst's needs. As mentioned earlier in this chapter, integration time and, for classical spectrometers, PMT voltage are two parameters that are often selected to fit the needs for a specific application or analysis.

Instrument Calibration

Before a sample is analyzed and the elemental concentrations of interest can be determined, the instrument must be calibrated. This is done by creating a calibration curve (function) for the measurement of emission for standard solutions and a blank. When linear calibration curves are used exclusively, it is usually necessary to measure standards of only one concentration per element. Use of nonlinear curves requires more standards and is, therefore, more time-consuming. Because ICP-OES calibration curves are generally linear over four to six orders of magnitude of concentration, the use of nonlinear curves is negligible compared to their use in atomic absorption techniques where linearity is generally limited to two or three orders. The exception is for simultaneous ICP-OES instruments where a less sensitive line may not be available to extend the working range of the instrument for an element.

When a great deal of accuracy is not required for an analysis, the analyst may turn to a semiquantitative calibration routine. These routines, available under a wide variety of names, use calibration curves or factors that are created at an earlier time, perhaps weeks or months before the analysis, and stored by the system computer. For some programs, one or more standards may be used to normalize the calibration curve before the analysis begins. An ICP-OES system calibrated in this fashion can usually turn out results with an accuracy of $\pm 25\%$, depending on the number of standards used, the reproducibility of the operating conditions, and other factors.

Samples Analysis

Once the instrument has been calibrated, samples can be analyzed for the elements of interest. (For simultaneous ICP-OES systems, just prior to analyzing samples, the instrument should be checked for wavelength accuracy to assure that instrument drift has been compensated for - this is generally known as reprofiling or mercury recalibration (Hg recal).) Most of the decisions that need to be made to perform the actual analysis have been covered in the previous sections. Therefore, the part of the methodology concerned with this step is usually straightforward. The main decisions to be made are whether or not to use an autosampler for introduction of the samples and how often to recalibrate the instrument before running more samples. While the use of an autosampler is up to the discretion of the analyst, the frequency of recalibration may not be. Specified analysis protocols may dictate the frequency of the recalibration based on the results obtained from the analysis of "check" samples of known concentrations. Also, the stability of an instrument in a particular environment may partially determine how often the instrument must be recalibrated.

Report Generation

The final step in the ICP-OES analysis methodology is the generation of a report that lists the concentrations of the elements of interest along with other information deemed necessary by the analyst or the specified analysis protocol. Since most ICP-OES instruments available today are operated from external computers, the flexibility for computerized report generation is usually quite extensive. Third party software is often used for creation of specialized reports such as those required by the U. S. Environmental Protection Agency. The analyst should determine what the specific reporting needs are for the analyses to be performed and act accordingly.

Correcting for Spectral Interferences in ICP-OES

Spectral interferences (also referred to as background interferences) encountered in ICP-OES fall into four different categories. These categories are simple background shift, sloping background shift, direct spectral overlap, and complex background shift. Each of these interferences has its own causes and remedies.

Simple Background Shift. The most common type of spectral interference encountered in ICP-OES and fortunately the easiest to correct is the *simple background shift*. This interference is defined as a shift in background intensity that is essentially constant over a given range, 0.5 nm for example, on either side of the analyte line. The background may shift either up or down.

Figure 4-4 shows an example of a simple upward background shift. The lower scan in this figure was obtained by introducing an aqueous solution containing 5.0 mg/L of tungsten into an ICP-OES instrument and then scanning across a 0.25 nm spectral range centered on the analyte wavelength. The only prominent spectral feature in this scan is the tungsten analyte emission line at 207.911 nm. The upper scan was obtained by introducing an aqueous solution containing 1000 mg/L of aluminum and scanning across the same spectral region using the same analytical conditions. The high concentration of aluminum emits a continuum of radiation in the given wavelength range.

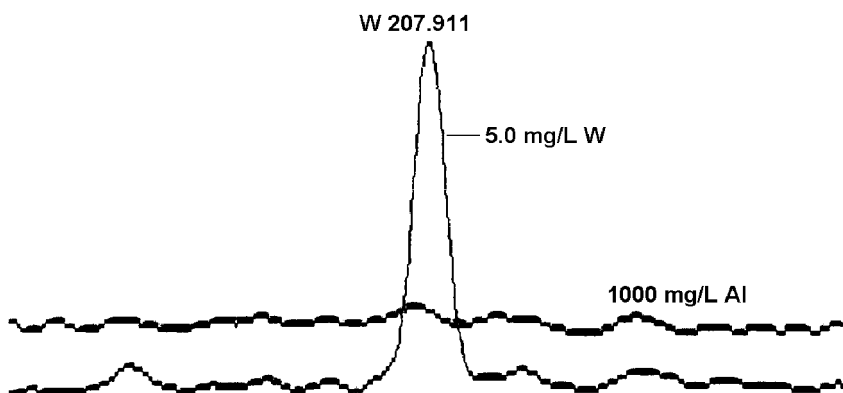


Figure 4-4. Simple background shift caused by 1000 mg/L aluminum at the tungsten 207.911 nm line.

The effect of the aluminum continuum is to increase the level of the background emission in the vicinity of the tungsten line. Unless the extra background emission due to the aluminum is corrected for, the determination of the tungsten concentration in an aluminum alloy using this wavelength would have a significant positive error associated with it. Fortunately, the intensity of the aluminum continuum can be automatically measured and then subtracted from the intensity measurement at the tungsten wavelength to correct for the interference. To do this, a *background correction point* would be selected somewhere near, but not falling on, the profile of the tungsten line as is shown in Figure 4-5. An alternative to background correction in this particular case would be the selection of a different emission line for tungsten that is not affected by the aluminum continuum, as is shown in Figure 4-6.

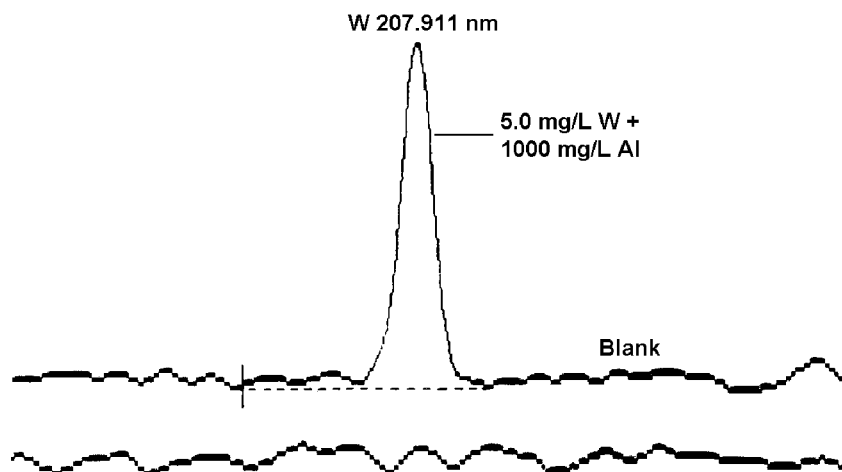


Figure 4-5. Single-point background correction for the simple background shift caused by 1000 mg/L aluminum at the tungsten 207.911 nm line.

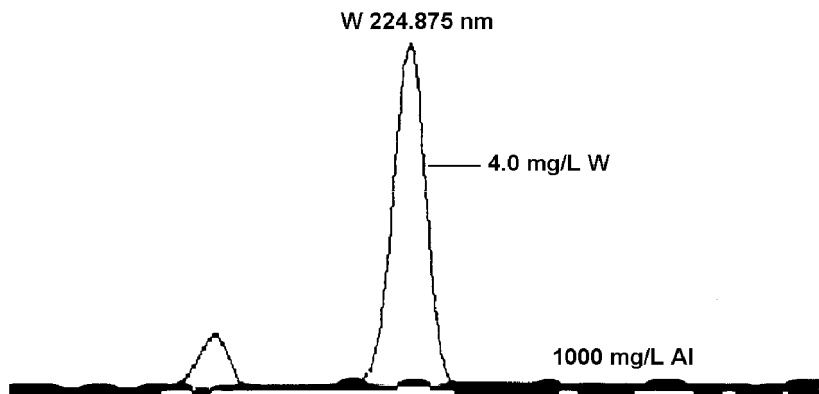


Figure 4-6. No background shift is caused by 1000 mg/L aluminum at the tungsten 224.875 nm line.

Sloping Background Shift. An example of an upward *sloping background shift* is shown in Figure 4-7. In the presence of a high concentration of aluminum, the cadmium line at 214.438 nm is overlapped by one wing of a severely broadened aluminum line nearby. This wing overlap causes an upward sloping positive background shift at the cadmium analyte line.

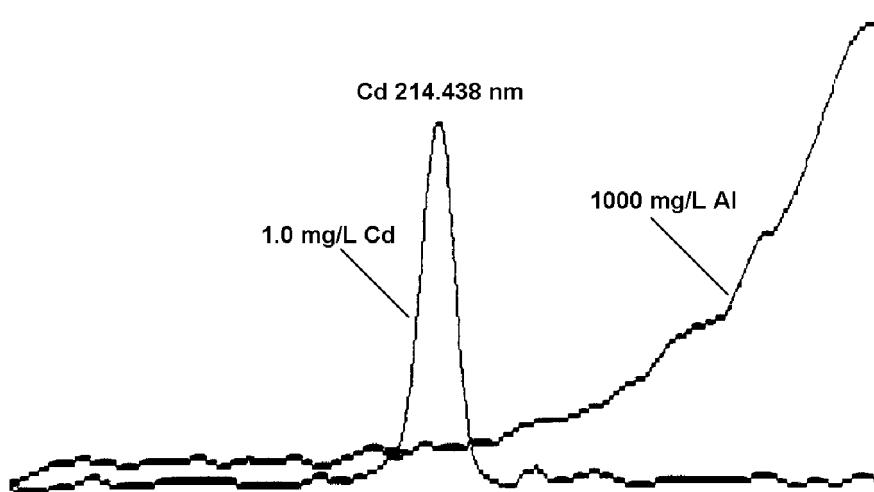


Figure 4-7. Aluminum background spectrum representing a sloping background shift at the cadmium 214.438 nm line.

Since the slope of the Al emission line wing is constant on either side of the cadmium line, two background correction points are used to correct for the sloping background shift. As shown in Figure 4-8, these points are selected with one point on each side of the cadmium peak.

The cause of a sloping background shift is usually the presence of a very intense atomic or ionic emission line that has been broadened either by a high concentration of that element in the sample or by the presence of electric fields in the plasma (known as Stark broadening). Another possible cause of a sloping background shift is from the molecular emission bands sometimes present in the ICP discharge, especially when the plasma is not shielded from the ambient atmosphere.

Direct Spectral Overlap. No two elements have an atomic or ionic emission line that is at exactly the same wavelength as any other element. At first glance, this statement would seem to preclude the possibility of obtaining a direct spectral

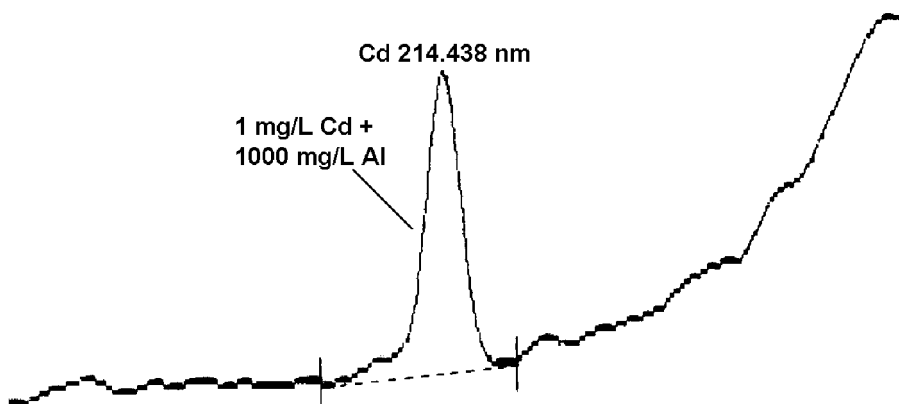


Figure 4-8. Two-point background correction for the sloping background shift caused by 1000 mg/L aluminum at the cadmium 214.438 nm line.

overlap, where an interfering emission line falls directly upon the analyte emission line. This is not the case, however, because each spectral line has a finite spectral width and because all measurement systems are imperfect. Since the exit slits used in monochromators and polychromators have finite widths, the light measured at the detector actually comes from a small range of wavelengths. Thus, there is no known way to observe one and only one wavelength of light. Because of this limitation, two lines may appear to be overlapped when they are both within the spectral bandpass of the spectrometer.

High resolution optical systems certainly limit the effects of spectral overlap. As the resolving power of the spectrometer is increased, the number of lines that can cause a spectral overlap interference will decrease. However, even when high resolution spectrometers are used, it is not always possible to avoid direct spectral overlaps, especially for polychromator-based systems that may not have alternate wavelengths available.

Figure 4-9 shows an example of a direct spectral overlap. If an alternate line is not available for the analysis, it still may be possible to correct for the interference using a technique called *interelement correction* (IEC). In the IEC technique, the contribution of the interfering element to the analyte emission intensity is corrected by measuring the emission intensity of the interfering element at another wavelength and applying a predetermined correction factor to the results. For simultaneous

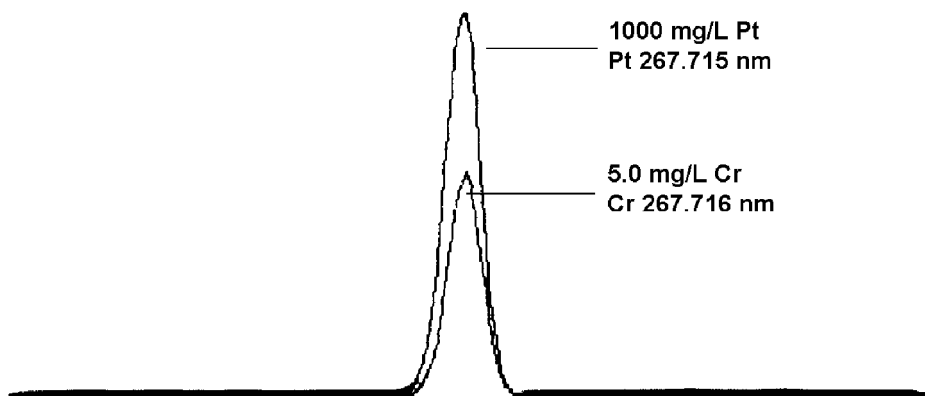


Figure 4-9. Direct spectral overlap caused by a platinum matrix at the chromium 267.716 nm line.

ICP-OES instruments, IEC is used to the extent where the technique assumes that each spectral wavelength measured in an analysis responds to all elements, each element with its own sensitivity. (In practice, the situation is not quite as bad as it might seem because many of the sensitivities will be essentially zero.) Use of the IEC technique in this way requires that at least one emission line be measured for each interfering element suspected to be in the sample. For samples of reasonable complexity, calibration becomes a tedious process. Also, for polychromator-based instruments with a limited number of channels, it may not be possible to correct for certain interfering elements. With advanced detector systems, all spectral lines are present, so interelement correction is possible.

Unless the difference in the wavelengths of the overlapping lines is less than about 0.002 nm, interfering element correction is generally not useful for correction of direct spectral overlaps when using a sequential ICP-OES instrument that scans over the analyte emission line to locate the peak. The IEC technique may, however, be useful to correct for those simple, sloping and complex background shifts that can be directly attributable to a specific element.

Complex Background Shift. A *complex background shift* is represented by a shift in a background intensity that varies significantly on either side of the analyte line. This interference is usually caused by the occurrence of a number of intense, closely spaced emission lines nearby, and perhaps directly overlapping, the analyte

wavelength. An example of a complex background shift is shown in Figure 4-10. While the automatic background correction features available on some state-of-the-art ICP-OES instruments may be used to correct for some of these interferences [12], it is usually advisable to use an alternate wavelength for the element experiencing the interference.

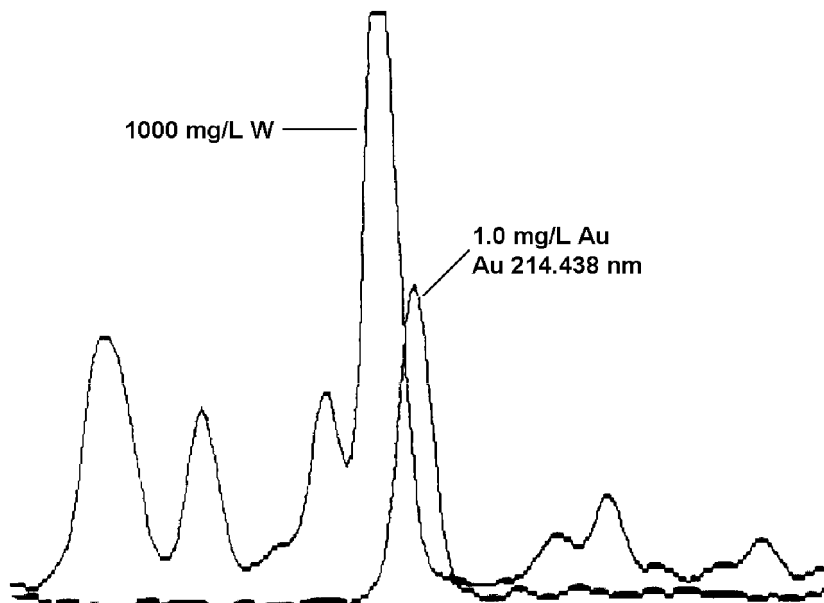


Figure 4-10. Tungsten matrix spectrum causing a complex background shift at the gold 267.595 nm line.

A fifth type of "interference" that is also spectral in nature warrants brief mention, even though it does not meet the definition of an interference given earlier in this chapter because it is the same for both standards and samples. These are *absorption interferences*. Absorption interferences arise when part of the emission from an analyte is absorbed before it reaches the detector. There are two causes of absorption interferences in ICP-OES. One, which has already been mentioned, is the absorption of emission below 190 nm by the oxygen in a nonvacuum or nonpurged spectrometer. The other effect is observed when the concentration of a strongly emitting element is so high that the atoms or ions of that element that are in the lower energy state of the transition of interest absorb significant amounts of the radiation emitted by the excited atoms or ions. This effect, known as *self-absorption*, is usually what determines the upper end of the linear working range for a given emission line. Emission lines and working ranges should be chosen to avoid these absorption interferences.

Other Spectral Interference Correction Techniques. There are some other possible ways to overcome or control some of the spectral interferences mentioned. One way is to prepare standards so they also contain the interfering elements found in this sample, making sure that the concentrations of these elements are the same in all solutions. Thus, when Cr standards are being prepared for analysis of a steel sample, the analyst would make the standards with the same concentration of the other elements expected to be in the sample. This is clearly a tedious procedure and requires that standards be specific for a particular sample. It also requires that the concentration of the other elements be known as well as being reasonably constant in the samples.

Many analysts, especially those working with atomic absorption techniques, use the standard additions method as a panacea for interference correction. While it is possible to correct for some interferences in ICP-OES by using standard additions, the amount of time and effort required for the technique, compared to other correction techniques, has limited its use in ICP-OES.

Multiple emission line determinations have also been used to overcome problems with spectral interferences. Unless one is trying to make determinations near the detection limits of the technique, there are usually several lines that can be used for determination of a single element. It is unlikely that spectral interferences would be the same for each of these lines. Therefore, if the concentrations derived from the intensities of several lines agree, the analyst can be reasonably certain that there are no spectral interferences. If the concentrations do not all agree, the analyst may be able to eliminate those results that seem to have an interference. The traditional form of interelement correction (IEC) uses intensity measurement at the analyte emission wavelength and compares the emission intensity of the interfering element with the analyte. This works quite well as long as the concentration of the interfering element remains within the linear concentration range, the matrix remains constant and the plasma conditions remain constant. A better, more accurate method for performing spectral interference corrections uses the wealth of information obtained with advanced detector systems and is known as *Multicomponent Spectral Fitting* (MSF)¹⁴.

Ordinary IECs attempt to correct for interferences by making a single measurement of the interferent and, from that, creating a mathematical factor that is applied to subsequent measurements of the analyte. MSF, rather than relying on a simplistic assumption, measures not only the interferent but also the background contribution from the matrix, thereby creating a correction formula. The result is an improvement in accuracy and detection limits. MSF utilizes a multiple linear least squares model based on an analysis of the pure analyte, the matrix and the blank as illustrated in Figure 4-11. MSF creates an interference-corrected mathematical model and

allows the determination of the analyte emission in a complex matrix with improved detection limits and accuracy.

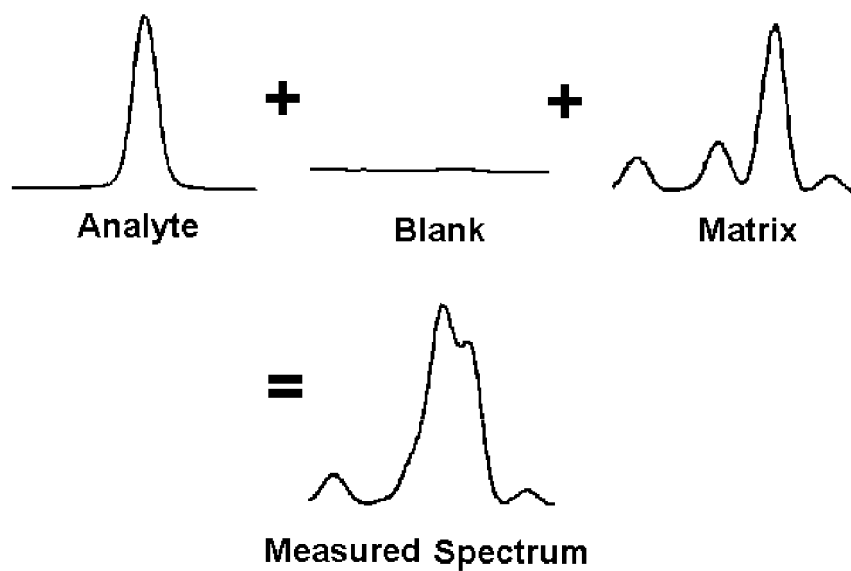


Figure 4-11. Components of the emission spectrum.

5 ICP-OES APPLICATIONS

The versatility of ICP-OES makes it a good analytical technique for a wide variety of applications. This versatility is due not only to the large number of elements that can be determined rapidly at trace levels but also to the wide variety of sample types that can be analyzed using the ICP-OES technique.

In this chapter, ICP-OES applications have been grouped into six generalized categories: Agricultural and Foods, Biological and Clinical, Geological, Environmental and Waters, Metals, and Organics. While an exhaustive review of each of these application areas is beyond the scope of this book, some examples of ICP-OES applications are discussed to give the reader an idea of the types of analyses where this technique has been used successfully.

Information regarding general application areas and specific applications can be obtained from a number of sources. Unfortunately, there is no one source that contains all the information needed to perform any and all ICP-OES analyses. For general discussions of applications, the books about ICP-OES by Boumans; Monstaser and Golightly; and Thompson and Walsh are very good (see table 5-1).

For reviews of the latest ICP-OES applications, see the Fundamental and Applications Reviews published in alternating years in the journal *Analytical Chemistry*. The Fundamental Reviews are categorized according to technique, e.g., Emission Spectrometry. The Applications Reviews are categorized according to sample Related Drugs. The *Journal of Analytical Atomic Spectrometry* contains applications reviews in its "Atomic Spectrometry Updates" section. These reviews are a good starting place to search for references to specific analyses reported in the chemical literature. Also quite useful in locating literature references to specific applications are computer data base search services, such as CAS Online, available through various outlets. The journal *Atomic Spectroscopy* also publishes a biannual bibliography of atomic spectroscopy-related articles.

Detailed information about specific applications can be found in a number of sources. The ICP-OES books by Boumans and by Thompson and Walsh, while not exhaustive references, provide detailed information on some selected applications. Many monographs, such as "Selected Methods of Trace Metal Analysis" by J. C. Van Loon, also contain detailed methodology for several analyses. Journals on

Table 5-1
References for ICP-OES Applications

General applications

"Inductively Coupled Plasma Emission Spectroscopy - Part 2", P. W. J. M. Boumans, ed., *Chemical Analysis*, Vol. 90, P. J. Elving, J. D. Winefordner, eds., John Wiley & Sons, New York, 1987.

"Inductively Coupled Plasmas in Analytical Atomic Spectrometry", A. Montaser and D. W. Golightly, eds., 2nd Edition, VCH Publishers, Inc., New York, 1992.

"A Handbook of Inductively Coupled Plasma Spectrometry", M. Thompson and J. N. Walsh, Blackie, Glasgow, 1983.

Application Reviews

"Fundamental Reviews", *Analytical Chemistry* **60**, (1988). (published in even-numbered years)

"Applications Reviews", *Analytical Chemistry* **59**, (1987). (published in odd-numbered years)

"Atomic Spectrometry Updates", *Journal of Analytical Atomic Spectrometry*, various issues.

Representative Journals

Analytical Chimica Acta

Analytical Chemistry

The Analyst

Applied Spectroscopy

Atomic Spectroscopy

Clinical Chemistry

Journal of Analytical Atomic Spectrometry

Journal of the Association of Official Analytical Chemists

Spectrochimica Acta, Part B

Talanta

chemistry and related topics contain the greatest amount of detailed information about specific analyses. Table 5-1 contains a list of several such journals. While few organizations have the resources to subscribe to every journal containing papers on ICP-OES application, access to these journals is often available through university libraries and various cooperative loan programs.

Agricultural and Foods

The ICP-OES technique has been applied to the analysis of a large variety of agricultural and food materials. Types of samples include soils, fertilizers, plant materials, feedstuffs, foods, animal tissues, and body fluids. Analyses of these materials are required to determine levels of essential nutrients as well as levels of toxic elements in the materials.

Most agricultural and food materials are generally not in the form of dilute aqueous solutions nor are they readily soluble in distilled water. Therefore, analyses of these materials by ICP-OES often requires that rigorous sample preparation procedures be carried out prior to analysis. Fortunately for the analyst, the use of modern microwave sample digestion techniques is helping to simplify the sample preparation steps for agricultural and food materials as well as many other sample types.

Some typical applications of ICP-OES in this area include determination of trace metals in beer and wine; analysis of infant formula for Ca, Cu, Fe, Mg, Mn, P, K, Na and Zn; determination of country origin of orange juice through trace element analysis; determination of 14 elements in peanuts; and analysis of soils for toxic metal contamination.

Biological and Clinical

As research reveals more information regarding the roles and behaviors of trace elements in biological systems, ICP-OES has become an important tool in the area of biological and clinical applications. Determinations by ICP-OES of essential, toxic and therapeutic trace elements are important in the medical research laboratories as well as in the clinical and forensic lab environments.

Of significant concern regarding trace element determinations in the biological and clinical fields is the contamination of samples prior to their analysis. While it is always important to consider sources of contamination when performing trace determinations in any field, the biological and clinical area is particularly susceptible to errors due to contamination originating in the sample collection and sample preparation steps. The use of surgical equipment, such as scalpels, needles, scissors, and forceps, often contaminates the sample with trace quantities of the very elements being determined in the sample. For this reason, appropriate equipment should be

used to collect, process and store biological and clinical samples before analysis by ICP-OES.

Many biological and clinical samples are either too small or contain elemental concentrations too low for ICP-OES analysis using conventional pneumatic sample introduction. In these cases, it is often necessary to turn to alternate sample introduction techniques such as ultrasonic nebulization, electrothermal vaporization, or hydride generation, or preconcentration techniques such as ion exchange or solvent extraction.

Examples of ICP-OES analyses of biological and clinical samples include determinations of Cr, Ni and Cu in urine; Al in blood; Cu in brain tissue; Se in liver; Cr in feces; Ni in breast milk; B, P and S in bone; and trace elements in oyster and tuna tissues.

Geological

Geological applications of ICP-OES involve determinations of major, minor and trace compositions of various rocks, soils, sediments, and related materials. The major use of ICP-OES in this field is for prospecting purposes. The technique is also used for applications such as determining origins of rock formations and for marine geochemistry.

Preparation of geological samples for analysis by ICP-OES often involves the use of lithium metaborate fusion reactions, especially for materials containing high levels of silica. Acid dissolutions are also commonly used for many geological materials. Of major concern for geological applications of ICP-OES is the elimination of residues that may be present following acid digestion or dissolution of a fusion bead. Careful selection of the nebulizer used with the ICP instrument can help to reduce problems caused by high salt and residue concentrations.

Typical applications of ICP-OES for analysis of geological samples include determination of U in ore grade material; analysis of river sediments for several metals; analysis of carbonate drill cores for major, minor and trace elements; determination of rare earth elements in rock formations; and analysis of plankton for several elements.

Environmental and Waters

The area of environmental analysis is quite a broad topic, covering many different types of ICP-OES applications. Many of these applications, such as analyses of soils, sediments, and animal and plant tissues, overlap areas covered previously in this chapter and will not be addressed in this section. This still leaves a number of

important environmental ICP-OES applications, not the least of which are the analyses of various types of water. Other important environmental ICP-OES applications include analyses of sewage sludge, domestic and industrial refuse, coal and coal fly ash, and dust and other airborne particulates.

The analysis of water can be the simplest of all ICP-OES applications, depending on the type of water being analyzed and the required measurement levels and protocols. Fresh waters generally require only that the sample be stabilized with a mineral acid before analysis by ICP-OES. Some waters may require filtering to remove particulates. For analyses requiring very low detection levels, it may be necessary to perform some kind of preconcentration step prior to analysis. Ultrasonic nebulizers are also useful for improving sensitivity for such analyses. Analyses of sewage sludge, various refuses, and coal and coal fly ash require more rigorous sample preparation while collection of airborne particulates requires use of air filtering techniques.

Examples of environmental ICP-OES applications include various water quality analyses as required by the U.S. Environmental Protection Agency; determination of Fe, Cd, Cu, Mo, Ni, V, and Zn in seawater; determination of phosphorus in municipal wastewater; determination of heavy metals in inner-city dust samples; and trace metal analysis of coal fly ash.

Metals

ICP-OES is used widely for the determination of major, minor and trace elemental constituents in metals and related materials. The technique is used for analysis of raw materials, production control, and quality control for final products as well as in the developmental lab environment. Sample preparation is generally through acid digestions, except for oxide materials which often require use of fusion techniques. Analysis of metals is also the most likely use of solid sampling techniques such as spark or laser ablation with ICP-OES instruments.

A particular difficulty associated with metals analysis by ICP-OES is the potential for a large number of spectral interferences since many metals exhibit very complex emission spectra. Use of a high-resolution spectrometer and spectral interference correction techniques are often required for metals analyses by ICP-OES.

Some representative applications of ICP-OES for the analysis of metals and related materials include determination of toxic, trace and major constituents in coal and slags; analysis of low alloy steels for As, B, Bi, Ce, La, P, Sn and Ta; high-precision determination of Si in steels; determination of contaminants in high-purity Al; and analysis of superconducting materials for trace contaminants.

Organics

Analysis of organic solutions by ICP-OES is important not only for analyzing organic-based materials such as petroleum products but also for a wide variety of other applications. For many of the analyses from the other application categories discussed in this chapter, it is necessary to perform sample preparation in which the final form of the analyte is contained in an organic solvent. For example, solvent extraction for the purpose of preconcentrating analyte species is a widely used sample preparation technique for ICP-OES. Also considered under the category of organic analyses would be introduction of organic effluents and vapors from high performance liquid chromatography (HPLC) and gas chromatography (GC) separations.

While analysis of organics by ICP-OES is generally straightforward, there are often some special requirements. For example, introduction of organic matrices into the ICP discharge usually requires that the ICP be operated at a higher RF power than is normally required for aqueous samples. Sometimes it is also necessary to use special nebulizers or torch injector tubes. When a peristaltic pump is used to transport the sample to the nebulizer, special consideration must be made regarding the chemical resistance of the pump tubing used with respect to the organic solvent.

The analysis of used lubricating oils for trace metal content is one of the more popular applications for organics analysis by ICP-OES. Some other applications include analysis of solvent-extracted geological materials for trace elemental composition; determination of lead in gasoline; determination of Cu, Fe, Ni, P, Si and V in cooking oils; analysis of organophosphates for trace contaminants; and determination of major and trace elements in antifreeze.

APPENDIX A

INSTRUMENT MAINTENANCE AND PERFORMANCE VERIFICATION

While ICP-OES analyses are often simple to perform, obtaining good analytical results requires that a certain level of attention be given to details that could influence the outcome of the analyses. Besides preparing samples carefully and selecting the proper hardware and operating parameters, the analyst should make sure that the instrument is set up and maintained properly. The first part of this appendix offers some general guidelines and recommendations for proper instrument care and maintenance. The second part lists some general tests that can be performed to help assure the analyst that the instrument is functioning properly. More specific information on maintenance and performance tests can usually be found in the operator's manuals provided with commercial ICP-OES instruments.

INSTRUMENT CARE AND MAINTENANCE

Sample Introduction System and ICP Torch

The improper performance of a sample introduction system is one of the most common causes of poor precision and accuracy for an ICP-OES analysis. In general, the analyst should keep in mind that anything that prevents a smooth, consistent flow of sample to the ICP discharge can be a source of error for an analyses. Below are some simple guidelines for care and maintenance of an ICP torch and sample introduction system.

Cleanliness. Keeping the torch and sample introduction system clean and free from obstructions is important in assuring a smooth, uncontaminated flow of sample to the plasma. It is a good idea to run a blank solution through the sample introduction system for several minutes after an analysis is run or before the instrument is shut down for the day. If samples with a complex matrix have been run, it may be advisable to take the system apart for a more thorough cleaning.

Peristaltic Pump Tubing. Check for depressions or flat spots on the tubing. New pump tubing may require a short break-in period to stretch out to a consistent length. This break-in period can be minimized by manually stretching the tubing a few times

before it is placed onto the peristaltic pump head. Make sure that the pump tubing used is appropriate for the sample type.

Nebulizer. Make sure that the nebulizer is not clogged or leaking. The sodium bullet test described in the second part of this appendix is often used as a quick check of the nebulizer. When making visual observations of the aerosol to check for a uniform spray pattern, be sure that this is done using a noncorrosive liquid (deionized water is recommended) and that proper eye protection is worn.

Drain System. The drain system should be filled with liquid to the level that will provide the proper backpressure for the inner or nebulizer gas flow. Sample waste that is drained from the spray chamber should flow smoothly through the drain system; uneven flow often indicates the need for cleaning or a kink or other restriction in the drain line.

Torch. Check for leaks that can be caused by cracks or other damage to the quartz tubes, O-rings or gas fittings. Accumulated deposits on the torch should be removed. When analyzing solutions containing high levels of particulates or dissolved solids, the injector may become clogged and should be removed and cleaned. When analyzing organic-based solutions, it may be necessary to remove carbon deposits periodically from the torch and injector.

RF Generator

The RF load coil should be inspected occasionally for signs of corrosion or leakage. The high-voltage wires, rods and other components of the plasma initiation system should also be inspected occasionally and replaced if corroded or worn. It may also be necessary to clean the filters over the air intakes if fans are used to cool the generator electronics. The power amplifier tubes used in most RF generator designs sometimes need to be replaced, but this should be only be done by a qualified service engineer.

It is important to always make sure that the laboratory exhaust venting system for the ICP torch box is functioning properly before igniting the plasma. Harmful ozone, toxic combustion products and metal fumes may accumulate in the laboratory if not vented properly.

Spectrometer

Spectrometers generally require little maintenance. Purge windows should be regularly inspected and carefully cleaned or replaced if necessary. The electronics section of the spectrometer may also have air filters that should be cleaned when

needed. Some sequential scanning instruments employ wavelength calibration routines that should be run periodically as recommended by the manufacturer.

Computer

Computer maintenance should not be left out of the instrument maintenance regime. Besides taking care of the computer hardware by cleaning floppy disk drives and air filters, backup copies of all important software and data files should be regularly maintained. If data files are stored on hard disk, the user should occasionally "clean up" the data file directories by erasing files or moving them to floppy disks or tape. It is a good idea before starting an analysis to make sure that there is sufficient space remaining for data storage on the floppy disk or hard disk to be used for this purpose.

VERIFICATION OF INSTRUMENT PERFORMANCE

It is usually advisable to check the performance of an instrument before an analysis is started. In some cases, such as certain environmental analyses, the stated analysis protocol may specify performance tests that must be run before, during and after an analysis. Such protocols are often quite rigorous, since the validity of the data produced from the analysis must be able to stand up in a court of law if it is challenged.

Some general tests that are often used to verify that an ICP-OES instrument is performing properly are listed below. Some of these tests are quite simple and should be performed on a daily basis. Other tests are more rigorous and can be used as diagnostic tests should the analyst suspect that the instrument is not functioning properly. Users may find it helpful to keep records of their test results as trends or patterns in the results may help to diagnose problems with an instrument. However, the user should be aware of what variability is expected for test results before assuming that a change in a result indicates an instrument problem.

It should be noted that the user should generally wait for an ICP-OES system to be warmed up properly before performing these tests. Recommended warm-up times are usually provided by the instrument manufacturer and are typically 30 to 60 minutes.

Visual Bullet Test

This is a simple test that can often be performed on a daily basis. In this test, the user introduces a solution containing 1000 mg/L or more of an element whose atom emission produces a well-defined "bullet" in the center of the ICP discharge. The mere presence of the bullet indicates that sample aerosol is reaching the plasma

while the vertical position of the bullet in the discharge is an indicator of the gas flow and RF power settings being used. Sodium and yttrium are often good elements to use for this test.

Signal Intensity

The number of emission counts for a given concentration of an element is often used as a quick instrument diagnostic. It is usually more useful for trend analysis than as an absolute indicator of performance since the emission counts may vary somewhat from day to day.

BEC

The background equivalent concentration (BEC) is an indicator of relative sensitivity for an emission line. A BEC of a higher than normal value often indicates problems with the efficiency of the sample introduction system, although it can actually be due to a number of causes.

Precision

The short-term precision obtained for several (5-10) measurements for a strong emission line is often used as an indicator of the noise associated with sample introduction. The precision is usually expressed as % CV (coefficient of variation) or % RSD. The precision for an argon emission line is sometimes used as a diagnostic for the RF generator.

Detection Limits

Detection limits are often used as the ultimate tests of instrument performance since they combine measurement of sensitivity with measurement of noise. Detection limits by themselves, however, are not very good diagnostic indicators. If the measured detection limits are not within their expected ranges, there could be several different causes. Detection limits are best used for diagnostic purposes when combined with a series of other, more specific tests.

Ion/Atom Ratio

Many ICP users employ a ratio of the emission intensity of an ion line to the emission intensity of an atom line as a diagnostic indicator of the relative excitation conditions in the plasma. Because such ratios are usually sensitive to RF power, inner or nebulizer flow and viewing height, they can be used to ensure that an equivalent combination of these parameters is used for an analysis. Running an analysis under

a specific set of conditions can be vital when predetermined factors, such as IEC coefficients or stored calibration curves, are used in an analysis.

Wavelength/Peak Alignment

Because all dispersive UV/visible spectrometers are subject to some degree of drifting, it is important to be sure that the spectrometer is calibrated properly in terms of wavelength before an analysis. For some instruments, this is done automatically by the instrument software at the beginning of an analysis. Other instruments, mainly polychromator-based instruments with refractor plate spectrum shifters, may require manual adjustment of the wavelength drive mechanism.

APPENDIX B

GLOSSARY

The following is a glossary of terms commonly used in analytical atomic spectrometry.

Absorption interference - an interference caused by the absorption of analyte emission before it reaches the detector.

Accuracy - the closeness of a measured result to the actual value.

Acid digestion - process of dissolving a sample in an acid matrix, usually accompanied by heating.

Aerosol - a fine mist of droplets created by a nebulizer.

Analog-to-digital (A/D) converter - an electronic device whose input is an analog signal, such as voltage or current, and whose output is a digital value proportional to that signal.

Analyte - the species whose presence is detected or concentration is determined in an analysis.

Array detector - a silicon chip that is manufactured with a one or two-dimensional array of photosensitive material on its surface. The photons that are absorbed by the units (*pixels*) of the array are converted to electrons which are collected and read out. Examples include Photodiode Arrays (*PDAs*), Charge-coupled Devices (*CCDs*), Charge-injection devices (*CIDs*), and Segmented-array Charge-coupled Devices (*SCDs*).

Aspiration - process whereby a high-speed gas flow is directed across an open tube, creating a negative pressure and thereby drawing solution through the tube.

Atomic absorption spectrometry (AAS) - elemental analysis technique that uses absorption of electromagnetic radiation to detect the presence of the elements of interest.

Atomic emission spectrometry (AES) - elemental analysis technique that uses atomic emission of electromagnetic radiation of neutral atoms or ions to detect the presence of the elements of interest.

Atomic spectrometry (AS) - class of elemental analysis techniques that use the absorption, emission or fluorescence of electromagnetic radiation of atoms or ions to detect the presence of the elements of interest.

Atomization - process of dissociating vaporized sample molecules into free atoms.

Atom transition - emission from or absorption by an atom.

Auxiliary argon flow - see Intermediate argon flow.

Axial plasma - a horizontal ICP which is viewed from the end; i.e., through the tail plume into the normal analytical zone (NAZ), or axial-viewing.

Babington nebulizer - a type of high solids nebulizer in which the aerosol is created by flowing the liquid over a spherical surface that contains an orifice from which a high speed gas flow emanates.

Background correction - Process of correcting the intensity recorded for a particular wavelength for intensity due to the ICP continuum background and other *spectral interferences*. This is normally done by choosing one or two points at one or both sides of the peak you want to correct. Points can be chosen manually or automatically. The software then measures the intensity at these points, interpolates an intensity at the peak wavelength, and then subtracts that intensity from the intensity recorded at the peak.

Background correction point - designated wavelength at which a measurement is taken to be used for subtracting background contributions from an emission signal.

Background equivalent concentration (BEC) - the concentration of a solution that results in an analyte emission signal equivalent in intensity to that of the background emission signal at the measurement wavelength. Used as a relative indicator of sensitivity in ICP-OES. The lower the concentration of this solution, the more sensitive the instrument for that element.

Background shift - any change in the emission intensity at an analyte wavelength that is not due to the analyte.

Blank solution - a solution that does not contain a detectable amount of the analyte of interest. Typically used for calibration purposes.

Calibration curve - a plot, equation (function) that describes the relationship between the concentration of an analyte and the variable that is measured to indicate the presence of the analyte. Once determined, this relationship can be used to determine the analyte concentration in a sample. In atomic emission spectrometry, a plot of emission intensity versus concentration is normally used for this purpose.

Calibration function - see Calibration curve.

CCD - see Charge-coupled Device.

CGN - Concentric glass nebulizer. See Concentric nebulizer.

Charge-coupled Device (CCD) - A two-dimensional array detector that uses a charge-coupled readout of the photoelectrons generated by light absorption. See *also* Array detector, SCD.

CID - see Charge-injection Device.

Charge-injection Device (CID) - A two-dimensional array detector that uses a charge-injection readout of the photoelectrons generated by light absorption. See *also* Array detector.

Coefficient of variation (CV) - used as measure of relative precision for a group of measurements, it is the standard deviation divided by the mean. Often expressed as a percent. Also known as relative standard deviation (RSD).

Collisional transition - a change in the energy state of an atom or ion caused by a collision with another particle.

Concentric - to have a common center.

Concentric nebulizer - a type of nebulizer in which the aerosol is created by flowing a high-speed gas and a liquid through a pair of concentric tubes that have their open ends in the same proximity.

Coolant argon flow - see Outer argon flow.

Correlation coefficient - indicates the quality of the fit between the calibration curve and the points it is fitting. A value of 1.000 indicates a perfect fit.

CRDL - Contract Required Detection Limits for the U.S. EPA Contract Laboratory Program.

Cross-flow nebulizer - a type of nebulizer in which the aerosol is created by flowing a high speed gas perpendicular to the open end of a capillary tube through which the liquid is directed.

Crystal-controlled generator - a class of radio frequency (RF) generators that use an oscillating crystal source to define and control the frequency of operation.

Decay - any process in which an excited atom or ion changes to a lower energy state.

Demountable torch - any of several designs of ICP torches in which the three concentric tubes are not permanently sealed together.

Desolvation - process of removing the solvent molecules from a sample droplet, resulting in a dried sample particle.

Detection limit - concentration of an analyte that results in a signal intensity that is three times the standard deviation of the background intensity at the measurement wavelength. (Some definitions may use two times the standard deviation of the background.) Used to indicate the smallest concentration at which the analyte can be detected with a specified degree of certainty.

Detector - a photosensitive device that absorbs photons and converts them into electrons with a certain efficiency. These photoelectrons can be measured to indicate the intensity of the incoming light, that is, the number of photons from the emission source. See *also* Array detector, CCD, CID, and SCD.

Diffraction grating - an optical device, consisting of a mirror with many finely spaced grooves etched or ruled onto its surface, used to disperse light according to wavelength and spectral order.

Direct current plasma (DCP) - a high temperature discharge that is created by a high density direct current flowing through a conductive gas between a set of two or three electrodes.

Direct injection - a sample introduction technique in which a liquid sample stream is introduced directly into the center of the plasma discharge.

Direct insertion - a sample introduction technique in which a solid sample is packed into an electrode that is then inserted into the center of the plasma discharge.

Dispersion - a measure of the separation, in angle or space, of different wavelengths of light by a diffraction grating. "Angular dispersion" describes the separation by angle, and "linear dispersion" describes the separation in space. See Reciprocal linear dispersion.

Dynode - one of the intermediate stages in a photomultiplier tube that amplifies the signal by emitting more secondary electrons than it collects.

Echelle grating - coarsely ruled diffraction grating used in multiple orders to achieve high spectral *resolution*.

Electromagnetic radiation - form of energy that can be described as particles or waves whose wavelengths range from gamma rays to very long radio waves, including visible light.

Electrothermal atomization (ETA) - use of a heated graphite tube or metal strip to desolvate, vaporize and atomize a sample for atomic spectrometry.

Electrothermal vaporization - use of a heated graphite tube or metal strip to desolvate and vaporize a sample for atomic spectrometry.

Emission intensity - the measurement of the amount of light at a given wavelength emitted from a spectral source. Usually expressed in relative, as opposed to absolute, units.

End-on plasma - see Axial plasma.

Energy level - one of the allowed states in which a system can exist. As applied to electrons in atoms, it indicates the energy corresponding to a given electron orbital.

Energy transition - any process in which an electron of an atom or ion is transferred to a different energy level.

Entrance slit - a narrow slit through which light enters a spectrometer.

Excitation - a process in which an electron is promoted to a higher energy level, resulting in an atom or ion said to be in an excited state.

Excitation characteristics - the amount of energy required to promote an electron to a higher energy level in an atom or ion. This excited state is necessary for the atom or ion to emit light. Different elements have different excitation characteristics.

Excited state - an energy state of higher energy than the ground state of the system.

Exit slit - a narrow slit through which light exits a spectrometer.

Focal length - the distance from the focal point of a lens or curved mirror to its principal point. In a spectrometer, this is usually the distance from the entrance slit to the first collimating optic. In general, the longer the focal length of a spectrometer, the greater the linear dispersion.

Free-running generator - a class of radio frequency generators that use the electronic constants of their circuit components to determine and control the frequency of operation without the use of external triggers such as an oscillating crystal unit.

Fusion reaction - a sample preparation technique in which an insoluble solid sample is reacted with another compound to create a soluble solid.

Grating density - the number of lines or grooves per unit length on a diffraction grating, usually expressed as lines/mm or grooves/mm. The higher the grating density, the greater the dispersion of the light diffracted by the grating.

Ground state - the most stable, lowest energy state of a system. In a ground state atom or ion, all electrons are in their lowest energy levels.

High solids nebulizer - a class of nebulizers capable of continuously nebulizing solutions containing high levels of dissolved solids.

Hydride generation - a sample introduction technique in which the analyte is reacted with atomic hydrogen to form a volatile hydride of the analyte, allowing for more complete introduction of the analyte into the atomization source.

IEC - see Interement Correction.

Induction region (IR) - the region of an ICP discharge into which the radio frequency (RF) energy is coupled.

Inductive coupling - process of transferring energy to a system through the use of electromotive forces generated by magnetic fields.

Inductively coupled plasma (ICP) - a high-temperature discharge generated by flowing a conductive gas through a magnetic field induced by a load coil that surrounds the tubes carrying the gas.

Inductively coupled plasma-mass spectrometry (ICP-MS) - an elemental analysis technique that uses an ICP to desolvate, vaporize, atomize, and ionize a sample and mass spectrometry techniques to detect and measure the sample ions.

Initial radiation zone (IRZ) - the region of an ICP discharge where excited analyte species first begin to emit their characteristic radiation which comprises mainly emission from neutral atom transitions.

Injector - the centermost tube of an ICP torch through which the sample aerosol is introduced to the plasma. Usually made of quartz or ceramic materials.

Inner argon flow - the flow of argon gas that is directed through the nebulizer and carries the sample aerosol through the injector and into the plasma. Typically 0.5 - 2 L/min. Also known as Nebulizer argon flow and Sample argon flow.

Integration time - the length of time for which a measurement is taken at a specific wavelength. In a scanning spectrometer, it is usually given as the measurement time for each point that is measured across a defined spectral region.

Interelement correction (IEC) - a spectral interference correction technique in which emission contributions from interfering elements that emit at the analyte wavelength are subtracted from the apparent analyte emission after measuring the interfering element concentrations at other wavelengths.

Interference - anything that causes the signal from an analyte in a sample to be different from the analyte signal for the same concentration of that analyte in a single element calibration solution.

Intermediate argon flow - the flow of argon gas that is contained between the intermediate and center (injector) tubes of an ICP torch. Typically 0 - 2 L/min. Also known as Auxiliary argon flow.

Internal reference - IUPAC name for *internal standard*.

Internal standard (IS) - a nonanalyte element, present in all standards, blanks and samples, that is used in conjunction with an internal standardization technique. Also known as an *internal reference*.

Internal standardization - a technique that uses the signal from an internal standard element to correct for interferences in an analysis.

Ionization - process where a neutral atom is converted to a charged ion through the gain or loss of an electron.

Ionization potential - the amount of energy needed to remove an electron from an atom or ion that is in its ground state.

Ion transition - emission from or absorption by an ion.

IR - see Induction region.

IRZ - see Initial radiation zone.

IS - see Internal standard.

IUPAC - International Union of Pure and Applied Chemistry.

IUPAP - International Union of Pure and Applied Physics.

Lateral plasma - a normal or vertical plasma which is viewed from the side or side-on viewing. Also known as a *radial plasma*.

Linear dynamic range - the range of concentrations over which calibration curves for an analyte are linear. Extends from the detection limit to the maximum linear concentration.

Linear fit - Type of *calibration curve* where a straight line is drawn through the standard and blank emission/concentration values.

Load coil - a length of tubing (typically 1/8-in. dia. copper) wound around the end of an ICP torch and connected to the RF generator. Used to inductively couple energy from the RF generator to the plasma discharge.

Matrix - the components of the sample other than the elements of interest. The matrix can substantially change results obtained through *spectral interference* or viscosity change.

Matrix matching - an approach to interference correction in which the major chemical compositions of the standards, blanks and samples are made identical, thereby canceling out the effect of the sample matrix on the analysis results.

Matrix-induced interference - interferences of a nonspectral nature that are caused by the sample matrix.

Maximum linear concentration - the highest concentration for an analyte that will result in a linear emission signal response.

Microwave induced plasma (MIP) - a high-temperature discharge created by coupling microwave energy into a conductive gas by any of a number of methods.

Mixed standard - a calibration solution that contains more than one analyte element.

Monochromator - a type of spectrometer used to isolate one wavelength of light at a time.

MSF - see Multicomponent Spectral Fitting.

Multicomponent Spectral Fitting (MSF) - a processing mode that distinguishes analyte spectra from interfering spectra by the use of stored mathematical models. It uses a multiple linear regression technique to fit the models created to unknown spectra during the analysis. Since only the peak shapes need to remain constant, typically, the models are independent of concentration, plasma conditions and matrix effects.

Multielement analysis - an analysis in which the concentration of more than one element is determined.

Nebulization - process of creating an aerosol from a liquid by the use of pneumatic or mechanical forces.

Nebulizers - a device used to create an aerosol from a liquid.

Nebulizer argon flow - see Inner argon flow.

Normal analytical zone (NAZ) - the region of the ICP discharge from which most of the analytically useful analyte emission originates.

One-piece torch - an ICP torch in which all three concentric tubes are permanently sealed together.

Optical emission spectrometry (OES) - elemental analysis technique that uses emission of electromagnetic radiation to detect the presence of the elements of interest.

Order - see Spectral order.

Outer argon flow - the flow of argon gas that is contained between the outer and intermediate tubes of an ICP torch. Typically 7 - 15 L/min. Also known as Coolant argon flow and Plasma argon flow.

Optimization - process of determining the best conditions and/or parameters for an analysis.

Peak search - a technique commonly used with scanning spectrometers in which the wavelength for an analyte peak intensity measurement is optimized by scanning over the analyte peak during the analysis.

Peristaltic pump - a pump in which the fluid is pushed through a length of flexible tubing by waves of mechanical contractions, usually caused by a series of rollers that travel along the length of the tubing.

Photocathode - the first stage of a photomultiplier tube; its function is to emit electrons when it is struck by a photon.

Photomultiplier tube (PMT) - a very sensitive light detection device that produces an electrical signal proportional to the amount of light falling upon its photocathode. Utilizes several stages of amplification (dynodes) that successively multiply the number of electrons emitted from each stage so that very small amounts of light can be measured.

Photon - a massless particle of electromagnetic energy.

Pixel - unit of array detector whose output can be read individually.

Planck's equation - the equation that describes the relationship between energy and frequency or energy and wavelength.

Plasma - a state of matter usually consisting of highly ionized gas that contains an appreciable fraction of equal numbers of ions and electrons in addition to neutral atoms and molecules.

Plasma argon flow - see Outer argon flow.

PMT - see Photomultiplier tube.

Pneumatic nebulizer - a class of nebulizers that use high-speed gas flows to create an aerosol from a liquid.

Polychromatic light - electromagnetic radiation consisting of more than one wavelength.

Polychromator - a type of spectrometer used to isolate two or more wavelengths of light at the same time.

Precision - a statistical measure of the reproducibility of a set of measurements. Commonly used indicators of precision include standard deviation (SD), relative standard deviation (RSD) and coefficient of variation (CV).

Preheating zone (PHZ) - the region of the ICP discharge in which the majority of the sample is desolvated, vaporized and atomized.

Purging - method whereby a gas (usually nitrogen) is used to fill a spectrometer to remove ultraviolet radiation-absorbing oxygen from the light path.

Qualitative information - information about which analytes are present in a sample.

Quantitative information - information about how much of an analyte is present in a sample.

Radial plasma - see Lateral plasma.

Radiative transition - an energy transition in which a photon is absorbed or emitted.

Radio frequency (RF) - the frequency range generally in between the audio and infrared frequency ranges (3 kHz - 300 GHz).

Reciprocal Linear Dispersion (RLD) - a measure of the separation in space of different wavelengths of light by a diffraction grating usually expressed as nanometers per millimeter at the focal plane of an instrument. Grating instruments, except for echelle types, have nearly constant RLD over their usable spectral range. For echelle type instruments, the RLD is related to a specific wavelength.

RF power - the amount of energy per unit time transmitted from the RF generator to the ICP discharge. Usually measured in Watts.

Refractory compound - a chemical compound, usually metal oxides or carbides capable of existing at very high temperatures.

Refractory element - an element that, in its pure solid form, has a very high melting point.

Residence time - the amount of time that an analyte spends in a given region of an atomization/excitation source.

Resolution - a measure of a spectrometer's ability to separate two adjacent wavelengths. The most common use of the term is to indicate the smallest difference between two adjacent wavelengths at which they can be distinguished from one another. While technically incorrect, the term is often used interchangeably with "spectral bandpass" or "spectral bandwidth". See also "Spectral bandpass" and "Resolving power."

Resolving power - the average wavelength of two equally strong lines that are just adequately separated, divided by the difference in the two wavelengths. Also known as Resolution. See Resolution and Spectral bandpass.

Sample argon flow - see Inner argon flow.

Sample matrix - the major chemical components of a sample.

SCD - see Segmented-array Charge-coupled device Detector.

Search window - the wavelength region around an analyte peak that is scanned when a peak search routine is used for sequential ICP instrumentation.

Secondary electron - an electron emitted by a photocathode or dynode in a photomultiplier tube.

Segmented-array Charge-coupled device Detector (SCD) - a specialized type of array detector developed for and used in the Perkin-Elmer Optima 3000 that has groups of photosensitive pixels, called *subarrays*, on the detector surface where important atomic emission lines appear. The SCD uses charge-coupled readout like a CCD, but the subarrays can be individually addressed. See *also* Array Detector, Detector, CCD.

Self-absorption - the absorption of intense analyte emission by atoms or ions of that same analyte element within the plasma. Occurs at high analyte concentrations and is generally responsible for determining the maximum linear concentration for strong analyte emission lines.

Sensitivity - analyte signal intensity per unit of analyte concentration.

Sequential analysis - multielement determinations performed by measuring one analyte signal at a time.

Side-on plasma - see Lateral plasma.

SIMAA - Multielement, simultaneous atomic absorption instrumentation.

Simultaneous analysis - multielement determinations performed by measuring several analyte signals at the same time.

Slit width - the width, usually in μm , of a spectrometer's entrance or exit slit.

Spectral bandpass - the difference of the minimum and maximum wavelengths that can pass through the exit slit of a spectrometer at a given time. The theoretical spectral bandpass can be calculated by multiplying the reciprocal linear dispersion by the slit width. The practical spectral bandpass has additional contributions from the diffraction width of the slit and the optical aberrations within the spectrometer. The lower the spectral bandpass, the greater the ability of a spectrometer to distinguish between two adjacent emission lines. Also known as spectral bandwidth.

Spectral interference - an interference caused by the emission from a species other than the analyte of interest.

Spectral order - area of a diffraction pattern when the phase differences for a given wavelength is a whole number.

Spectrometer - a device used to separate, isolate and measure light according to wavelength. Because the slits of a spectrometer have finite widths, it is not possible to measure a single wavelength of light using a spectrometer, but instead, a very small range of wavelengths is measured (see spectral bandpass).

Spectrometry - the use of spectroscopic techniques to obtain qualitative and quantitative information about a sample.

Spectroscopy - the field of study concerning the production, measurement and interpretation of electromagnetic spectra arising from the interactions of electromagnetic radiation with matter.

Spray chamber - a device, placed between a nebulizer and an atomization/excitation source, whose function is to separate the aerosol droplets according to their size and to smooth out fluctuations in the sample-carrying gas flow.

Standard solution - a solution with an accurately known concentration of analyte, typically used for calibration of an instrument.

Subarray - group of *pixels* on an *array detector* which are positioned to measure a small, specific wavelength range.

Tail plume - the region located at the top of an ICP discharge and whose emission mainly originates from atoms and molecules.

Tesla coil - an electrical device used to create a high-voltage spark; often used for igniting an ICP discharge.

Thermal transition - a change in the energy state of an atom or ion that is caused by a collision with another particle. Also known as a collisional transition.

Torch - a device consisting of three concentric tubes, the outer two usually made from quartz, that is used to support and introduce sample into an ICP discharge.

Toroid - a "doughnut" -shaped object; also, the *induction region* of an ICP discharge.

Trace analysis - designated as the determination of analytes whose concentrations in the original sample are in the range of 100 ppm to 0.1 ppb. Determinations of concentrations below 0.1 ppb are designated "microtrace", those below 0.1 ppt, "nanotrace", and those below 0.1 ppq, "picotrace".

Ultrasonic nebulizer - a nebulizer in which the aerosol is created by flowing the liquid across a surface that is oscillating at an ultrasonic frequency.

Ultratrace analysis - designated as trace analyses in which the original sample size is less than 100 μg .

U.S. E.P.A. - United States Environmental Protection Agency. Also known as U.S. EPA.

V-groove nebulizer - a type of high solids nebulizer in which the aerosol is created by flowing the liquid down a V-shaped groove that contains an orifice from which a high-speed gas flow emanates.

Vaporization - process of breaking down desolvated sample particles into a gas of sample molecules, usually by intense heating.

Viewing height - the vertical position in an ICP discharge from where the emission that is being measured originates; generally given as the number of mm above the top of the load coil.

Wavelength - the distance between two adjacent peaks of a monoenergetic electromagnetic wave.

Wavelength calibration - the process of determining the relation between the physical settings of a spectrometer and the wavelengths at which it takes measurements.

Working range - the range of concentrations over which accurate analyte determinations can be made.

APPENDIX C

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