Inductively Coupled Plasma Atomic Emission Spectroscopy

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General Use

- Simultaneous multielement analysis
- Quantitative and qualitative analysis for over 70 elements with detection limits in the parts per billion (ng/mL) to parts per million (μg/mL) range
- Determination of major, minor, and trace elemental components

Examples of Applications

- Composition of metal alloys
- Trace impurities in alloys, metals, reagents, and solvents
- Analysis of geological, environmental, and biological materials
- Water analysis
- Process control

Samples

- *Form*: Liquids, gases, and solids; liquids are most common
- *Size*: 5 to 50 mL of solution, 10 to 500 mg of solids
- *Preparation*: Most samples are analyzed as solutions; solutions can be analyzed as received, diluted, or preconcentrated as required; solids must usually be dissolved to form solutions; gases may be analyzed directly

Limitations

- Detection limits parts per billion to parts per million
- Cannot analyze for noble gases
- Halogens and some nonmetals require vacuum spectrometer and optics
- Sensitivity poor for alkali elements, especially rubidium; cannot determine cesium

Estimated Analysis Time

- Dissolution of solids in sample preparation may require up to 16 h
- Analysis may require minutes to several hours

Capabilities of Related Techniques

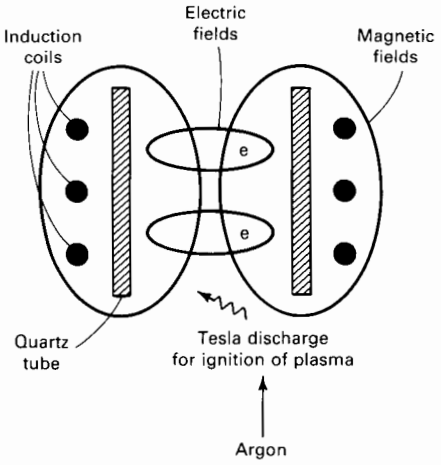
- *Direct-current arc emission spectrography*: Samples may be analyzed directly as solids; sensitivity and quantitative precision poorer; longer analysis time required
- *Atomic absorption spectroscopy*: Single-element analysis; better sensitivity for most elements, especially by using electrothermal atomization, but not as good for refractory elements; more limited dynamic range

Introduction

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique for elemental determinations in the concentration range of major to trace based on the principles of atomic spectroscopy. In theory, the technique applies to all elements except argon, and samples may be introduced as liquids, gases, or solids. In practice, favorable analytical results are obtained for approximately 70 elements, with detection limits usually attainable at the parts per billion level, and most samples are introduced in liquid form as aqueous solutions. The technique has found widespread application in the metallurgical, geological, environmental, agricultural, industrial, and biological fields and is an important technique in the modern analytical laboratory.

The first developmental research on the ICP as an excitation source for optical analytical atomic spectroscopy was published in 1964 (Ref 1) and 1965 (Ref 2). The first commercial instrumentation for analytical laboratories began to appear in the mid-1970s. In subsequent years, the success of the technique renewed interest in analytical atomic emission, which had been largely supplanted by developments in atomic absorption instrumentation in the 1950s and 1960s (see the article "Atomic Absorption Spectrometry" in this Volume). The success of the ICP was due to its ability to perform multielement analysis and to determine a wide concentration range in the same sample—two important characteristics atomic

Fig. 1 Electric and magnetic fields of the inductively coupled plasma

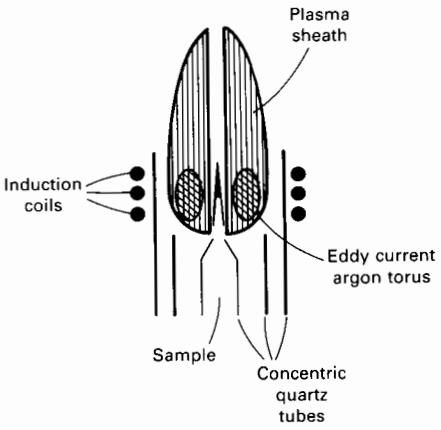


absorption could not match. The high-temperature and inert argon atmosphere of the plasma also greatly lessened the chemical and matrix interferences of flame emission techniques.

Principles of Operation

The ICP is an excitation source for atomic emission spectroscopy. It is an argon plasma operated at atmospheric pressure and sustained by inductive coupling to a radio frequency (RF) electromagnetic field. Argon gas flows axially through a quartz tube surrounded by three or four turns of an induction or work coil connected to an RF generator. The standard frequencies of operation are 27.12 MHz or, less commonly, 40.68 MHz, the frequencies allowed by the Federal Communications Commission for scientific and medical instrumentation. Power output is generally 1 to 5 kW.

Fig. 2 Structure of ICP plasma torch



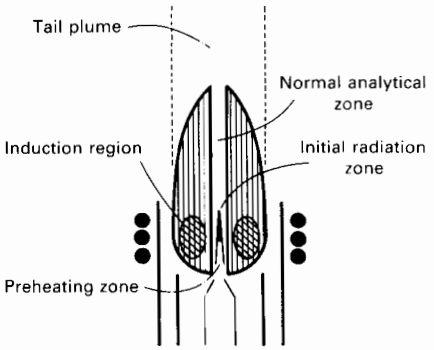
The high-frequency current of up to 100 A flows in the water-cooled copper induction coils, generating oscillating magnetic fields whose lines of force are oriented axially inside the quartz tube and follow closed elliptical paths outside the tubes. If free electrons are present inside the tube, the induced magnetic fields cause the electrons in the gas to flow in oscillating closed annular paths inside the quartz tube space. This electron flow is termed the eddy current, and the electrons are accelerated by the time-varying magnetic field, causing collisions that result in further ionization of the argon gas and resistive heating. These electrical and magnetic fields responsible for the plasma are represented in Fig. 1.

The energy transmission in the plasma is similar to an electrical transformer in which the induction coils are the primary winding and the ionized gas is the secondary. Because the argon gas is initially neutral and nonconducting, the plasma must be initiated by seed electrons, usually generated by a brief tesla discharge. With RF power applied, the plasma ignites instantaneously, then is self-sustaining. The resulting plasma is a highly ionized gas with temperatures in the proximity of 10 000 K.

The plasma torch is not a single quartz tube but three concentric tubes (Fig. 2). The high temperatures of the plasma require protective isolation from the quartz walls. This is accomplished by a tangential flow of coolant gas between the two outer tubes at a rate of about 15 L/min. This isolates the plasma from the torch walls and stabilizes and centers the plasma. This is sometimes referred to as Reed's vortex stabilization technique. An auxiliary gas flow known as the plasma gas is sometimes used during ignition of the plasma or with organic solutions. The plasma gas flows between the two inner tubes at 1 to 5 L/min. A small-diameter central tube is used to introduce the analytical sample into the plasma, usually as a fine liquid aerosol transported by a carrier gas flow at approximately 1 L/min.

Careful design of the torch enables the sample carrier gas to penetrate the base of the plasma so that the sample passes through a channel in the plasma central axis. The hot plasma is then toroidal, and the sample experiences a cooler central channel, with temperatures of 5000 to 8000 K. During a transit time of 2 to 3 ms in this central channel, the sample aerosol is desolvated, volatilized, dissociated, atomized, and, to varying degrees, ionized; the free atoms and ions are electronically excited. Radiation of varying wavelengths in the ultraviolet and visible portion of the spectrum is emitted on the nanosecond time scale as the electrons return to lower energy levels. The wavelength of this emitted radiation is characteristic of the atomic species present in the plasma and the intensity of the emitted radiation is proportional to the quantities of each atomic species present. Thus, analysis of the emitted radiation provides qualitative and quantitative elemental analysis.

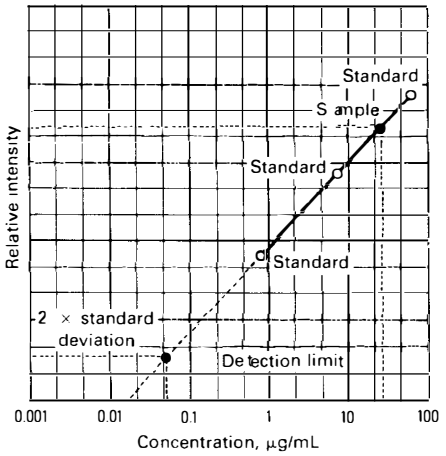
Fig. 3 Nomenclature of the zones of the inhomogeneous plasma



The ICP has a distinct structure (Fig. 3), and a nomenclature system has been derived to describe the zones of the plasma (Ref 3). Low in the plasma, predominantly atomic emission is observed. This initial radiation zone extends approximately 0 to 10 mm (0 to 0.4 in.) above the induction coils. Vertically higher, another region exists where predominantly ionic emission is observed. This normal analytical zone, the region most commonly used for spectroscopic measurements, extends approximately 10 to 20 mm (0.4 to 0.8 in.) above the induction coils. Higher still, the tail plume of the plasma extends 30 to 100 mm (1.2 to 4 in.) above the induction coils, where atomic and some molecular emission will be observed.

In the excitation temperature profile in the plasma, the temperature is moderate (~5000 K) in the lower zone, reaches a maximum (~6000 to 8000 K) in the normal analytical zone, then drops rapidly to lower values (<5000 K) in the tail plume (Ref 4). Because a temperature gradient exists in the plasma, different elements will reach their maximum emission intensity at different heights above the induction coils according to differences in excitation energies of the different atoms and ions (Ref 5). Therefore, in simultaneous multielement analysis, a compromise viewing height must be selected.

Fig. 4 Calibration curve for ICP analysis showing detection limits and concentration of analyte in sample



Analytical Characteristics

The ICP as an analytical technique provides the capability of performing simultaneous multielement analysis for as many as 60 elements within 1 to 2 min; applicability to most elements in the periodic table; a large linear dynamic range (calibration curves that are linear over three to six orders of concen-tration magnitude), enabling determination of trace, minor, and major components in a single analysis; detection limits in the parts per billion (ng/mL) range for most elements; precision and accuracy on the order of 1%; and relative freedom from chemical interfer-ences.

Detection limits for the ICP are determined by first establishing a calibration curve (plot of signal intensity at a given wavelength versus concentration for a series of standard solutions). The detection limit is calculated as the concentration that would correspond to an analytical signal equal to two (or three, according to choice of definition) times the standard deviation (noise) of repeated measurements of a blank at that wavelength (Fig. 4). This concentration is the lowest value measurable with any certainty as present in the sample. These detection limit values must be considered extreme limits, because they are determined under ideal situations. Practical detection limits will be somewhat higher. Some sample preparation procedures, such as dissolution and dilution, necessarily degrade the achievable detection limits of the elements in the original sample material.

Precision and Accuracy. The precision of the ICP technique is usually determined by making several consecutive measurements, then calculating the standard deviation of the replicates as a percentage of the mean value. Major causes of signal fluctuations in the ICP are small variations in the RF power applied to the plasma and changes in the nebulization process. Precision can be increased to less than 1% by close regulation of the RF power (most new instrumentation accomplishes this to $\pm 0.1\%$), by improved nebulization techniques, or by use of an internal standard. Nebulization is stabilized by using a mass flow controller to regulate the nebulizer gas flow and by use of improved nebulizer designs, such as the high-pressure crossflow nebulizer. The accuracy of the ICP technique is essentially limited by the precision and by systematic errors, such as interference effects, but is usually shown to be comparable to the precision.

Interference effects, sometimes termed matrix effects or interelement effects, are any phenomenon that interferes with the intensity versus concentration relationship of the analyte due to the presence of other components in the sample. Interference effects may be classified as spectral, vaporization-atomization, and ionization. Some causes in the latter categories may be physical or chemical.

Spectral interferences, a basic problem in any emission technique, arise from the incomplete isolation of radiation emitted by the analyte from other radiation as detected by the instrument. The emission spectra of many elements are complex, and the high temperatures of the ICP allow transitions from many excited states of the atom. Thus, the wavelength of the emission line selected for analysis may coincide with that of a line emitted by another component of the sample (direct spectral overlap), or the two lines may be so close in wavelength that they partially overlap (partial or wing overlap). If these close or coincident lines are not resolved at the detector, spectral interference occurs, and the intensity reading is erroneously high for the true concentration level.

Spectral interferences are fundamental problems in emission spectroscopy and will still occur for the ICP. Although partial overlaps may be reduced by using high-resolution spectrometers, direct spectral overlap necessitates selection of alternative

analytical wavelengths. The system computer, using interelement correction factors previously determined, can sometimes mathematically compensate for partial spectral overlap. The use of computer graphics in most new instrumentation assists detection and evaluation of spectral interferences. Using a graphics package, the immediate vicinity of an analytical line can be scanned and displayed on the computer terminal. Repetitive scans of analyte and suspected interferents at the wavelength of interest can be graphically overlaid and usually inspected for potential problems. Stray light in the spectrometer can also produce spectral interferences, but the use of holographic gratings and improved spectrometer design have greatly reduced this problem in new instruments.

Another type of spectral interference is continuum overlap caused by the electron recombination continuum that is part of the ICP background emission. This can be corrected by background subtraction from the analytical signal. However, one significant advantage of the ICP over flame and arc-spark techniques is the great reduction, due to high temperatures and inert argon atmosphere, in background emission arising from flame gases, combustion products, and molecular species.

Vaporization-atomization interference processes reduce the free atom population in the vapor phase and thus reduce the intensity of the emission signal. These can arise from various effects, such as the formation of refractory compounds, formation of metal oxides, or occlusion of analyte in refractory compounds formed by matrix components. These are major problems in flame spectrometry. The predominant absence of these interferences is a major advantage of ICP. The relatively long residence time of 2 to 3 ms combined with the high-temperature and argon atmosphere result in complete dissociation and atomization of the sample. Change in sample solution viscosity due to differing matrices or differing acid concentrations affect nebulization and alter the observed signal intensities. The chemical composition of the standards should be matched to those of the sample solutions to compensate for these interferences.

Ionization interferences result from a shift in the ionization equilibrium of the analyte or a modification of the excitation mechanisms due to the presence of other sample components, especially the easily ionized alkali elements. This is a common problem in flame systems. These effects are less severe but not absent (Ref 6) in the ICP, indicating the need to match standards and samples for optimum results.

Analytical Procedure

Inductively coupled plasma is, in practice, essentially a solution technique. Therefore, the sample to be analyzed must be prepared as a solution unless it originated as such (waters, and so on). The volume of solution required for analysis depends on the type of spectrometer to be used and the number of elements to be determined. For a polychromator, as many as 60 elements can be determined with less than 5 mL of solution, although replicate measurements or longer integration times will require correspondingly more solution. For a monochromator, determination of each element requires approximately 2 to 5 mL of solution; correspondingly more solution is required for replicates or longer integrations. Smaller sample volumes may be analyzed using such specialized techniques as discrete sample introduction.

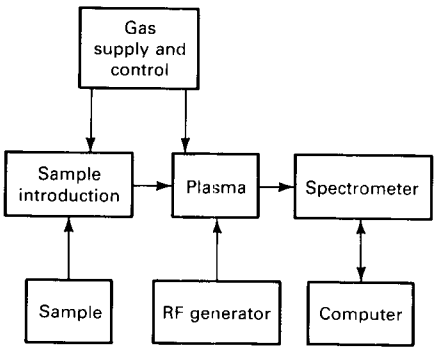
Once the sample has been prepared for analysis, it is necessary to calibrate the instrument by using a set of standard solutions of known concentration for each element to be determined. More than one element may be combined in a standard solution for efficiency if no interference effects are observed for the combination. In principle, it is possible to establish a calibration curve of signal intensity versus concentration using only a blank and one moderate concentration standard. However, use of a blank and two or three standard solutions that encompass the range of the expected sample values is preferable.

Calibration curves for the ICP are generally linear from approximately 10 ppb (ng/mL) to 1000 ppm (μg/mL), although self-absorption effects will cause curvature of the calibration curves for the alkali elements and some alkaline earths at 100 ppm and greater. These calibration curves remain analytically useful if enough standards were used to define the curves sufficiently. The instrument must be calibrated at least once daily; high precision and accuracy require more frequent calibration. In some cases, the alternation of samples and standards throughout the analysis is recommended for optimum results.

The sample is now analyzed by recording the signal intensity at the analytical wavelength for each element. In some cases, background subtraction is applied to correct for continuum radiation or sloping baseline in the spectrum. In other cases, interelement correction factors are applied for partial spectral overlap. These corrections and the final calculation of concentration from the predetermined calibration curves (Fig. 4) are done by the system computer.

Each element will have its own unique position of emission intensity maximum in the plasma. Further, each element will respond and optimize differently to changes in plasma parameters, such as power and gas flows. Nevertheless, an advantage of the ICP technique is that compromise conditions, which have become standard operating conditions in most analytical laboratories, exist that provide high-quality results for most elements simultaneously. The alkali elements, being the primary exception to this, may require special conditions for optimum results (Ref 6).

Fig. 5 Components in an ICP analytical system



System Components

The principal components of an analytical ICP system are (1) the sample introduction system, (2) the ICP torch and argon gas supplies, (3) the RF generator and associated electronics, (4) the spectrometer, (5) the detection electronics and interface, and (6) the system computer with appropriate hardware and software. The relationships among these components is shown in Fig. 5.

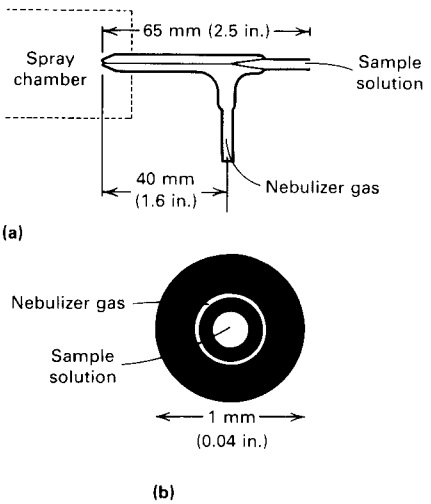
Sample Introduction

Although, in principle, samples for the ICP may be liquid, gas, or solid, in practice the predominant form of sample introduction into the plasma is solution. The most common method of introducing the solution is a fine aerosol of solution droplets generated by a pneumatic nebulizer.

Several nebulizer designs are used for the ICP. The two most frequently used pneumatic types are the concentric (Ref 7, 8) and the crossflow (Ref 9). Both designs depend on a high-velocity argon gas flow, termed the nebulizer or carrier gas, to create a low-pressure zone into which sample solution is drawn or pumped through a capillary tube and subsequently atomized into fine droplets of varying sizes by the force of the flowing gas. The size distribution of the droplets generally ranges from 0.1 to 100 μm in diameter. Only 10-μm or smaller

Fig. 6 Concentric or Meinhard nebulizer for ICP sample introduction

(a) Side view. (b) End view



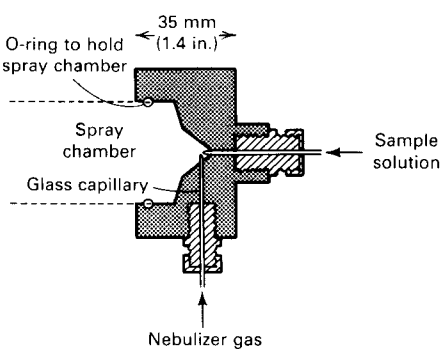
diameter droplets can be effectively desolvated, dissociated, atomized, and excited in the residence time of a few milliseconds in the plasma. Larger droplets contribute to excessively noisy analytical signals and cool the plasma by the introduction of too much water; they must be removed by passing the aerosol through a spray chamber after nebulization and before transport into the plasma by the carrier gas.

The concentric nebulizer, or Meinhard nebulizer, is illustrated in Fig. 6. It is constructed of borosilicate glass. Although variations are available, the basic model uses an argon flow of 1.0 L/min at a line pressure of approximately 275 kPa (40 psi) through an outer annulus as low pressure draws the sample solution through the inner capillary tube at approximately 1-2 mL/min. Even though these nebulizers perform well over extended times with dilute aqueous solutions, the fine dimensions of the sample capillary and the gas annulus make the nebulizer prone to blockage by small particles in the sample solution or the argon gas supply. Such blockages may stop sample and gas flows entirely or alter the flows, making detected signals erroneous in comparison to previous calibrations.

Another potential problem in using the concentric nebulizer involves sample solutions of high salts content. A phenomenon know as "salting up" may occur by which aspirated droplets deposit on the exterior of the nebulizer tip and evaporate, accumulating a dry deposit that partially blocks the tip and changes sample and gas flows. Many instruments incorporate means of reducing this problem by humidifying the nebulizer gas and washing the tip between samples. Stabilization of the analytical signal after beginning aspiration of a given solution requires approximately 20 s, known as the uptake delay. A 20-s delay is also required after stopping aspiration of the solution to clear the nebulizer and spray chamber.

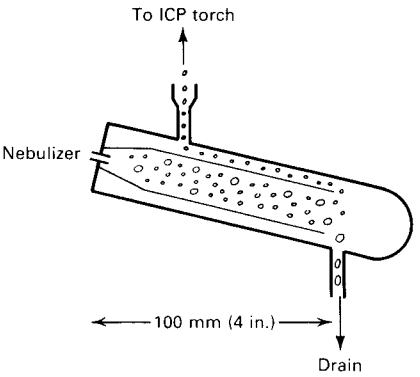
The crossflow nebulizer is the other most common pneumatic nebulizer design (Fig. 7). The sample capillary and the nebulizer gas capillary are mounted at right angles. The mounting may be fixed or adjustable. The adjustable mounting allows for optimization, but may be difficult to maintain for long-term stability or reproducibility. The horizontal gas flow creates a low-pressure zone over the tip of the vertical sample tube, drawing up sample solution that is shattered into fine droplets. Crossflow nebulizers are generally less subject to salting up than concentric nebulizers. The gas flow and solution uptake rates are similar, as is analytical performance. A fixed crossflow MAK nebulizer operated at 1380 kPa (200 psi) back pressure provides improved precision (Ref 10).

Fig. 7 Crossflow nebulizer for ICP sample introduction



Use of Peristaltic Pumps. Concentric nebulizers can initiate and sustain aspiration simply by the action of the nebulizer gas flow. This is true of some crossflow nebulizers. A peristaltic pump is commonly used to supply sample solution to either type of nebulizer. The peristaltic pump uses small-gage tubing to pass the solution along by a series of rollers on a rotating head. Typical rates are 0.8- to 2.0-L/min solution uptake and 2-Hz pump pulsation. Without use of the pump, the uptake rate of the sample solution will depend on the viscosity of the solution and the nebulizer gas flow rate. Changes in either will alter the amount of analyte reaching the plasma and can cause errors in the analytical measurement. The peristaltic pump will deliver solution to the nebulizer at a fixed volume rate and eliminate some of these errors.

Fig. 8 Spray chamber for ICP sample introduction



Spray Chambers. Once generated by the nebulizer, the aerosol passes into a spray chamber mounted just below the torch. The most common design is the Scott type illustrated in Fig. 8 (Ref 11). The spray chamber removes the larger droplets from the aerosol by forcing the aerosol to travel around a sharp bend in its path to the plasma. The larger, heavier droplets fall out or collide with the chamber walls and flow out of the drain in the bottom of the chamber. Because of the large distribution of droplet size, much of the aerosol flows out of the drain instead of upward into the plasma. The efficiency of a nebulizer is defined as the percent of aerosol reaching the plasma compared to the total solution uptake. For the pneumatic nebulizers described above, this efficiency is 1 to 5%.

Another design of spray chamber less frequently used causes the aerosol to strike a large impact bead placed in front of the nebulizer tip. This causes large droplets to fall out or break into smaller ones. Because pressure fluctuations in the spray chamber will change the observed analytical signal, a liquid trap must be provided in the drain line from the spray chamber and smooth flowing of the condensed liquid out of the chamber must be ensured.

Corrosion-resistant nebulizers and spray chambers are also available for analysis of solutions in concentrated acids, including hydrofluoric acid. Although most sample solutions for the ICP are prepared in aqueous or acidic mediums, such applications as extraction procedures in the sample preparation require the use of organic solvents. Introduction of organic solvents into the plasma can be accomplished with some modifications of the operating parameters, for example, operating at higher powers and use of the auxiliary plasma gas.