

Atomic Emission, Methods and Instrumentation

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Symbols

C_a	analyte concentration used to give I_a
I_a	intensity at certain analyte concentration and wavelength
I_{init}	intensity in presence of 1000 mg l^{-1} of the interfering species

Atomic emission spectroscopy is one of the most useful and commonly used techniques for analyses of metals and non-metals providing rapid, sensitive results for analytes in a wide variety of sample matrices. Elements in a sample are excited during their residence in an analytical plasma, and the light emitted from these excited atoms and ions is then collected, separated and detected to produce an emission spectrum. The instrumental components which comprise an atomic emission system include (1) an excitation source, (2) a spectrometer, (3) a detector, and (4) some form of signal and data processing. The methods discussed will include (1) sample introduction, (2) line selection and (3) spectral interferences and correction techniques.

Atomic Emission Sources

The atomic emission source provides for sample vaporization, dissociation and excitation. The ideal excitation source will allow the excitation of all lines of interest for the elements in the sample, and does this reproducibly over enough time to encompass full elemental excitation. Excitation sources include but are not limited to (1) inductively coupled plasma (ICP), (2) direct current plasma (DCP), (3) microwave-induced plasma (MIP) and (4) capacitively coupled microwave plasma (CMP). Glow discharges are utilized for direct solids analyses, but will not be discussed here. An analytical plasma is a high-energy, slightly ionized gas (approximately 0.01–0.1% ionized).

Inductively Coupled Plasmas

The most commonly used ion source for plasma spectrometry, the ICP, is produced by flowing an inert gas,

typically argon, through a water-cooled induction coil which has a high-frequency field (typically 27 MHz) running through it (Figure 1). The alternating current in the coil has associated with it a changing magnetic field which induces a changing electric field. The flowing gas is seeded with electrons by means of a Tesla coil. These electrons undergo acceleration by the electric field, and gain the energy necessary to excite and ionize the gaseous atoms by collision. This produces the plasma, self-sustaining as long as the RF and gas flows continue.

Sample particles entering the plasma undergo desolvation, dissociation, atomization and excitation. The ICP has sufficiently long residence times and high enough temperatures so that the sample solvent is completely vaporized, and the analyte reduced to free atoms, which undergo excitation. This excitation results in the emission of light at specific frequencies for elements in the sample, which is proportional to their concentration. An emission spectrometer separates the frequencies of light into discrete wavelengths, which are unique to given elements in the sample.

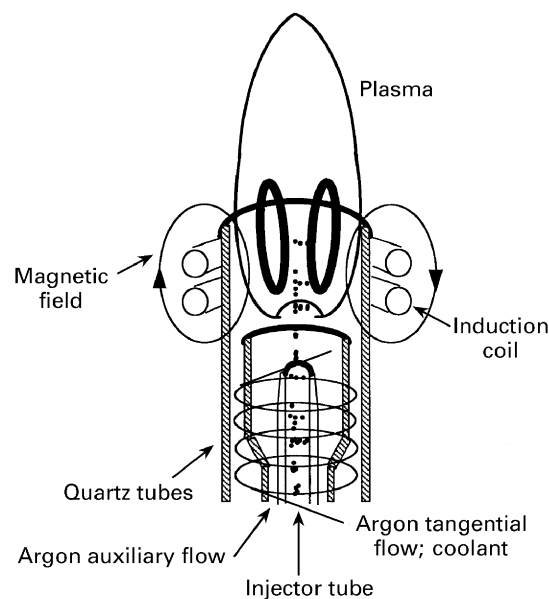


Figure 1 Inductively coupled plasma and torch schematic.

Direct Current Plasmas

In a DCP, a dc current passing between two electrodes heats the plasma gas, again typically argon, and produces a discharge. The most common version is the three-electrode system (Figure 2). This system has argon flowing around two graphite anodes and a tungsten cathode to produce the plasma. The sample is introduced between the anodes. Vaporization, atomization, ionization and excitation occur. This technique is more tolerant of samples containing a high proportion of solids than the ICP method. However, it is less efficient due to lower plasma temperatures, and the electrodes need to be replaced frequently.

Microwave-Induced Plasmas

A MIP is an electrodeless discharge generated in a glass or quartz capillary discharge tube, often in a resonant cavity. These tubes generally have an inner diameter of the order of a few millimetres, and the plasma gas is an inert gas such as helium or argon. The resonant cavity which is hollow and of the order of a few centimetres diameter, allows coupling of the microwave power into the plasma gas flowing through the capillary discharge tube. The microwave power supply operates at a frequency of 2.45 GHz. Microwave plasmas can be produced at atmospheric pressure, if the design of the cavity allows. Helium plasmas typically require reduced pressure unless a 'Beenakker cavity' is employed (Figure 3). MIPs use lower power levels (hundreds of watts) than those required by the DCP and ICP. However, due to the

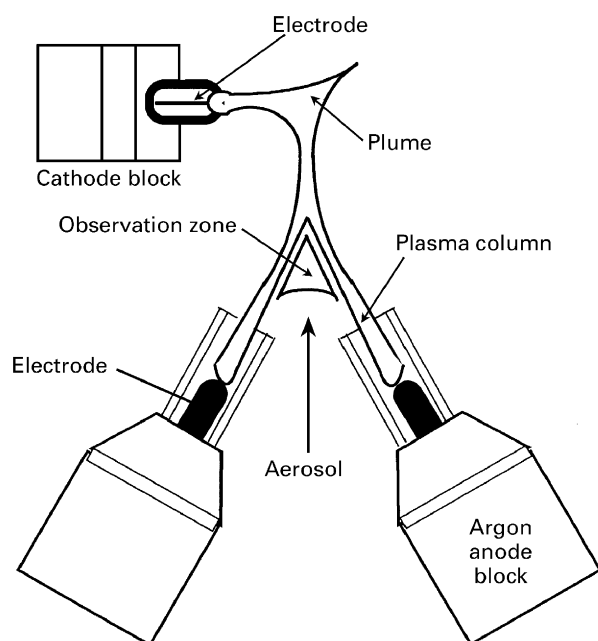


Figure 2 Direct current plasma schematic.

decreased size of the MIP, the power densities produced are comparable. Argon has an ionization potential of 15.75 eV, which is not sufficient in the argon ICP to produce the excitation ionization energy needed to ionize some elements efficiently, such as the non-metals. Helium plasmas are more efficient for these problem elements, as the ionization potential of helium is 24.6 eV. The MIP is not very adept at handling liquid samples due to the low powers employed. However, at higher powers above 500 W similar performance to the ICP may be obtained. The general lack of availability of these sources, as part of commercially available instrumentation, has limited their application and use.

Capacitively Coupled Microwave Plasmas

A CMP is formed using a magnetron to produce microwave energy at 2.45 GHz. This is brought to a hollow coaxial electrode via coaxial waveguides. The microwave power is capacitively coupled into the plasma gas, usually argon or nitrogen, via the electrode. This is an atmospheric pressure source with a small plasma volume. Power levels can range from 10 to 1000 W, with frequencies from 200 kHz to 30 MHz. Unlike other MIPs, the CMP is able to handle greater amounts of solvent. However, the CMP has been found to be easily contaminated due to the microwave energy being conducted through a coaxial waveguide to the electrode, which must be replaced regularly.

Spectrometers

The atomic emission source will produce unstable, excited atoms or ions, which spontaneously return to a lower energy state. The emission spectrum is produced when a photon of energy is generated during this transition. The basic assumption is that the emitted energy is proportional to the concentration of atoms or ions in the

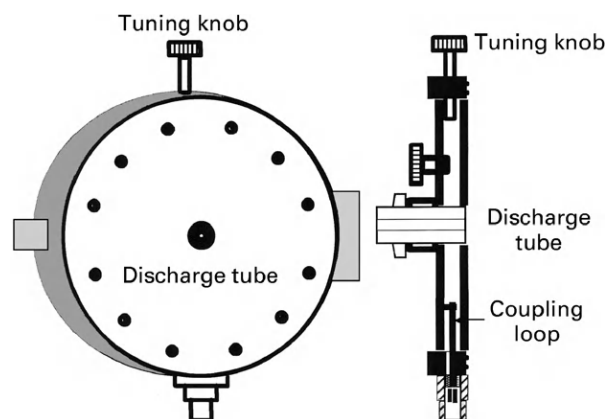


Figure 3 Microwave induced plasma schematic illustrating the 'Beenakker Cavity' design.

sample. The measurement of this energy is performed using the optics of the spectrometer to isolate the characteristic elemental emission wavelengths, and to separate this radiation from the plasma background. The spectrometer will need a high resolving power to be able to separate the lines of interest from the adjacent spectral lines (at least 0.1 nm). The spectrometer consists of (1) a dispersive element, such as a grating, and (2) an image transfer assembly which contains the entrance and exit slits, and mirrors or lenses.

The grating provides dispersion of the wavelength range of interest over a given angular range. Some commonly used grating spectrometers include (1) the Paschen–Runge spectrometer which is used in both sequential and simultaneous instruments and has the advantage of extensive wavelength coverage, (2) the echelle grating spectrometer, with excellent dispersion and resolution with a small footprint and (3) the Ebert and Czerny–Turner spectrometers which are similar except that the latter has two mirrors to the Ebert's one.

The slit allows a narrow line of light to be isolated. The number of lines will represent the various wavelengths emitted by the plasma, with each line corresponding to the image produced by the spectrometer slit, and each wavelength corresponding to a specific element. There are two slits used: (1) the primary slit through which light enters the spectrometer, and (2) the secondary slit through which light exits, producing a line isolated from the rest of the spectrum. The imaging system consists either of lenses or of concave mirrors.

One of the most useful aspects of atomic emission spectrometry is its capability for multi-element analysis. This can be achieved using either the sequential monochromator, where elements in a sample are quickly read one at a time, or the polychromator which allows the simultaneous measurement of the elements of interest.

Monochromators

Multi-element determinations using a monochromator must be sequential, as the monochromator can observe only one line at a time owing to single secondary slit. The slit can be set to scan the wavelengths, which is slower than in a simultaneous instrument, but allows for the selection of a wider range of wavelengths. A scanning monochromator uses a movable grating to find known individual spectral lines at fixed positions, typically a Czerny–Turner configuration. Although this allows the observance of only one individual wavelength at a time, it also allows all wavelengths in the range of the spectrometer to be observed.

Polychromators

Polychromators have a permanently fixed secondary slit for certain individual wavelengths (individual elements).

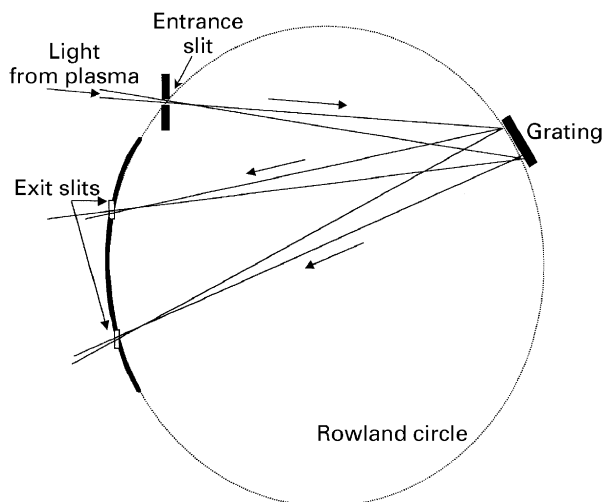


Figure 4 Beam path through a polychromator.

Each slit will have its own detector. This allows for truly simultaneous analyses of selected elements, resulting in much quicker analyses than the monochromator for elements that have a slit installed. However, the selection of possible analysis lines is limited. **Figure 4** shows a simplified diagram of the beam path in a polychromator. A polychromator can focus the emission lines on the circumference of the Rowland circle by using concave gratings; typically the Paschen–Runge configuration is used. In summary, the polychromator has a throughput advantage while the sequential scanning monochromator has flexibility as its advantage.

Detectors

Photomultiplier Tubes

A photomultiplier tube (PMT) consists of a photosensitive cathode, several dynodes and a collection anode. The dynodes are responsible for the increase in signal by electron multiplication. PMTs see the elemental line intensity per unit time proportionally with current and have wide dynamic ranges. A PMT, housed in a suitable mechanical movement, can scan the range of wavelengths in a spectrum sequentially, which involves longer analysis times. Alternatively, there can be a series of PMTs, each collecting the signal at discrete wavelengths at its assigned exit slit. Unfortunately, it always takes one PMT for each wavelength of light observed, whether the PMT is fixed or roving. Modern instruments have taken advantage of the advent of multichannel solid-state detectors to provide more flexibility in multielement analyses.

Charge-Coupled and Charge-Injection Devices

The charge-coupled and charge-injection devices (CCD and CID) are solid-state sensors with integrated silicon

circuits. They are similar in that they both collect and store charge generated by the light from the emissions in metal-oxide semiconductor (MOS) capacitors. The amount of charge generated in a charge transfer detector is measured either by moving the charge from the detector element where it is collected to a charge-sensing amplifier (CCD), or by moving it within the detector element and measuring the voltage change induced by this movement (CID). The CCD is susceptible to 'blooming' in the presence of too much light, since there can be an overflow of charge from a full pixel to an adjacent one. CCDs are best used in very sensitive, low light level applications. The CID does not suffer from 'blooming' due to its method of nondestructively measuring the photon-generated charge. The CID allows the monitoring of any wavelength between 165 and 800 nm, whereas the range of the CCD is between 170 and 780 nm.

Methods

Sample Introduction

Sample introduction into the plasma is a critical part of the analytical process in atomic emission spectroscopy (AES). Since the ICP is the most commonly used source, the sample introduction schemes described in the following sections will focus more on it than the other sources mentioned previously. Sample is carried into the plasma at the head of a torch by an inert gas, typically argon, flowing in the central tube at $0.3\text{--}1.5\text{ l min}^{-1}$. The sample may be an aerosol, a thermally or spark generated vapour, or a fine powder. Other approaches may also be taken to facilitate the way the analyte reaches the plasma. These procedures include hydride generation and electrothermal vaporization.

Torches

One of the torch configurations more commonly used with the ICP is shown in [Figure 1](#). The plasma torch consists of three concentric quartz tubes through which streams of argon flow. The nebulizer gas which carries the analyte into the plasma, flows in the central tube. The auxiliary gas flows around the central tube and adjusts the position of the plasma relative to the torch. The coolant gas streams tangentially through the outer tube, serving to cool the inside walls and centre of the torch, and stabilizes the plasma.

Nebulizers

The great majority of analyses in ICP AES are carried out on liquid samples. The most convenient method for liquids to be introduced into the gas stream is as an aerosol from a nebulizer. The aerosol may be formed by the action of a high-speed jet across the tip of a small

orifice or by the use of an ultrasonic transducer. A spray chamber is usually placed after the nebulizer to remove some of the larger droplets produced and thereby improves the stability of the spectral emission.

The most commonly used nebulizer designs are pneumatic and ultrasonic, although other types (electrostatic, jet impact and monodispersive generators) have been described. The selection of the appropriate nebulizer depends on the characteristics of the sample: mainly density, viscosity, organic content, total dissolved solids and total sample volume. Additionally, the performance of a particular nebulizer can be described using several attributes such as droplet size distribution, efficiency, stability, response time, tendency to clog and memory effects.

Concentric Nebulizers

Solution sample introduction has been associated with pneumatic nebulizers (concentric and cross-flow) almost universally for routine analysis due to their simplicity and low cost. However, they provide low analyte transport efficiency ($< 5\%$) to the plasma and may be prone to clogging.

The most widely used ICP nebulizer is the one-piece Meinhard concentric nebulizer ([Figure 5a](#)). It is a general-purpose nebulizer with low tolerance for total dissolved solids, used for applications requiring low nebulizer gas flows. It operates in the free running mode whereby the solutions are drawn up by the pressure drop generated as the nebulizer gas passes through the orifice. The viscosity of the solution and the vertical distance through which the liquid is lifted affect the rate of liquid transfer. Although the concentric nebulizer is easy to use, the transport efficiency is low, owing to the wide range of droplet sizes produced. In addition, nebulizer blockage may occur due to the presence of suspended solids becoming lodged in the narrow, central sample uptake capillary. Filtering or centrifuging the sample may minimize the risk of blockage. If a sample with a high dissolved-solids content dries in the nebulizer, it may also cause nebulizer blockage or interfere with the operation of the nebulizer by decreasing the signal. Frequent cleaning of the nebulizer solves this problem.

Cross-flow Nebulizers

The cross-flow nebulizer shows much of the same general behaviour of the concentric nebulizers. The cross-flow nebulizer is less prone to blockage and salting effects, although they may still occur as the sample solution passes through a capillary. The cross-flow nebulizer operates when a horizontal jet of gas passes across the top of a vertical tube ([Figure 5b](#)). The reduced pressure that is generated draws the liquid up the tube, where, at the top, it is disrupted into a cloud of fine droplets.

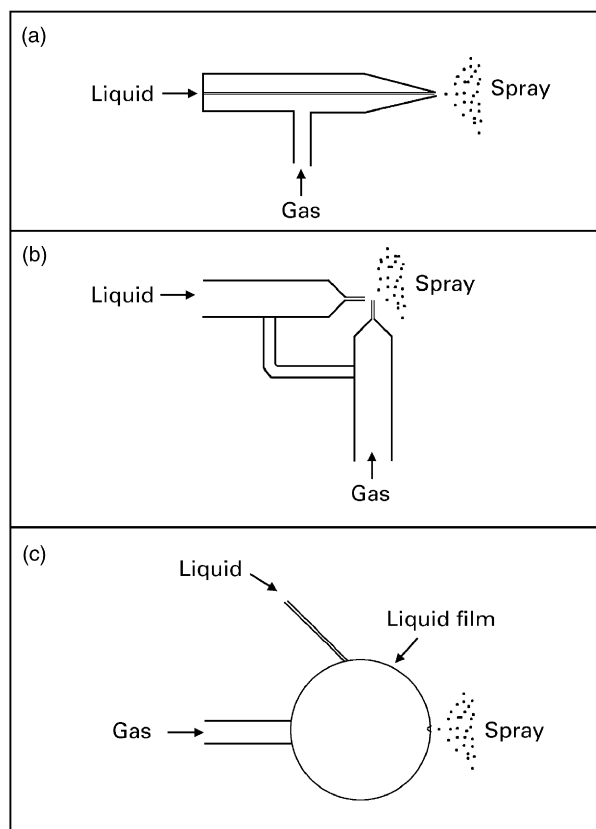


Figure 5 Schematic of the (a) concentric nebulizer, (b) cross-flow nebulizer, and (c) Babington nebulizer.

Babington-type Nebulizer

The Babington nebulizer is designed to allow a film of liquid containing sample to flow over the surface of a sphere (Figure 5c). A gas which is forced through an aperture beneath the film produces the aerosol. This design features the liquid sample flowing freely over a small aperture, rather than passing through a fine capillary, and is therefore more tolerant of high dissolved-solids. This kind of nebulizer can be used to introduce slurries into the system since the delivery of the sample is not constrained by a capillary. However, the Babington-type nebulizer shows extensive memory effects since the solution is allowed to wet the entire face of the sphere. A modification of the design is also in use, whereby the liquid sample passes through a V-groove and a gas is introduced from a small hole in the bottom of the groove. The main advantage of the V-groove nebulizer is its resistance to blockage. However, the design produces aerosol less efficiently, and it is of coarser size distribution than that produced by other concentric nebulizers.

Frit-type Nebulizer

The concentric and cross-flow nebulizers are inefficient at the 1 ml min^{-1} flow rate at which they usually operate,

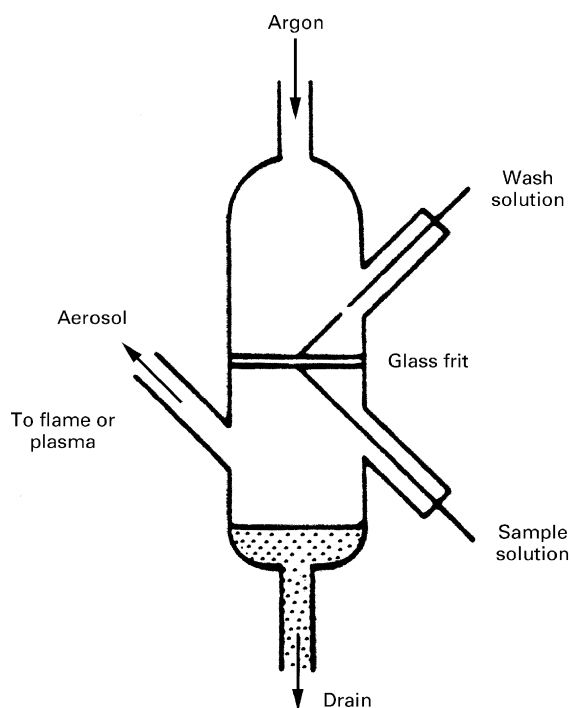


Figure 6 Glass frit nebulizer schematic. Reprint permission from Ingle JD and Crouch SR (1988) *Spectrochemical Analysis*. Englewood Cliffs, NJ: Prentice Hall.

producing only approximately 1% of droplets of the correct size to pass into the plasma. An alternative design is the frit nebulizer, which produces droplets with a mean size of $1 \mu\text{m}$. The glass frit nebulizer is depicted schematically in Figure 6. The sample flows over the fritted glass disc as the nebulizing gas is passed through the frit. This design provides an excellent fine aerosol, but at the expense of the fritted disc clogging over time. The transport efficiency is very high compared to the pneumatic-type nebulizers but the operation is at flows of $100 \mu\text{l min}^{-1}$ or less.

Ultrasonic Nebulizer

The ultrasonic nebulizer also produces fine aerosol and has a high sample-transport efficiency (Figure 7). The aerosol is generated when the solution is fed to the surface of a piezoelectric transducer which operates at a frequency between 0.2 and 10 MHz. Vibrations of the transducer cause the solution to break into small droplets which are then transported to the plasma. The ultrasonic nebulizer offers highly efficient aerosol production independent of the carrier-gas flow rate. With this nebulizer, more analyte can be transported into the plasma at a lower nebulizer gas flow rate than that seen with pneumatic nebulizers. This increases the sensitivity and improves detection limits since samples have a longer residence time in the plasma. However, the high

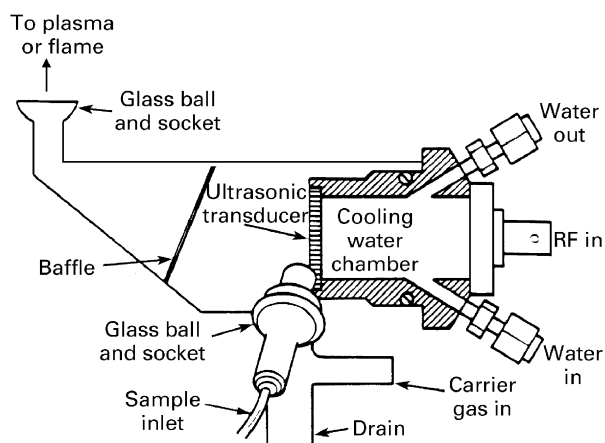


Figure 7 Ultrasonic nebulizer schematic. Reprint permission from Ingle JD and Crouch SR (1988) *Spectrochemical Analysis*. Englewood Cliffs, NJ: Prentice Hall.

efficiency also allows more water to enter the plasma, producing a cooling effect, which may decrease analyte ionization. Hence these nebulizers require desolvation to be realistically utilized. Apart from the analytical shortcomings of the ultrasonic nebulizer, the high cost of the commercial systems may be prohibitive.

Electrothermal Vaporization

Electrothermal vaporization can introduce liquid, solid, and gaseous (by trapping) samples to the plasma with high analyte transport efficiency (20–80%) and improved sensitivity over pneumatic nebulization. A small amount (5–100 μl) of sample is deposited into an electrically conductive vapourization cell (Figure 8). Initially, a low current is applied to the cell, which causes resistive heating to occur and dries the sample. A high current is then passed for a short time (typically 5 s) to completely vaporize the sample. An optional ‘ashing’ stage may be used to remove some of the matrix prior to the analyte vaporization stage. A stream of argon gas is passed through the unit and carries the sample vapour to the plasma. A variable current supply is required for controlling cell heating, and the sequence of heating steps is carried out using an electronic control system. Electrothermal vaporization allows sample matrix components, including the solvent, to be separated from the analytes of interest through judicious selection of temperature programming steps. This may reduce oxide formation and the number of spectroscopic interferences. Additionally, samples with high salt content and limited volume can be analyzed with electrothermal vaporization.

Hydride Generation

The problems associated with liquid sample introduction, and the inefficiencies in analyte transport can be overcome

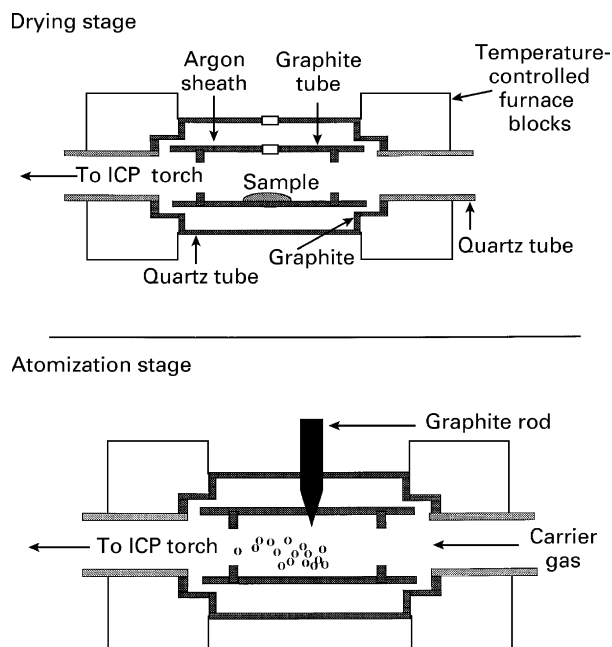


Figure 8 Illustration of electrothermal vaporization graphite furnace.

by presenting the sample in a gaseous form to the plasma. Introducing the analyte in a gaseous form eliminates the use of a nebulizer and a spray chamber. It also provides nearly 100% analyte transport efficiency, which subsequently improves the detection limits. Additional benefits include no blockage problems, the possibility of matrix separation and analyte preconcentration, and the absence of water, which reduces the levels of many polyatomic ion species. The hydrides of the elements arsenic, bismuth, germanium, lead, antimony, selenium and tin are easily formed in acidic solutions and are gaseous at room temperature. The most frequently used reaction is



where E is the hydride forming element of interest. Figure 9 shows an apparatus for hydride generation. It allows the mixing of the sample and the reducing agent, followed by the transport of the volatile analyte species (hydride) by the carrier gas to the plasma.

The gaseous sample introduction line is connected directly to the central tube of the plasma torch, eliminating the need for the conventional nebulizer and spray chamber. Additional equipment to handle gas mixing and dilution at controlled flow rates may be required.

Direct Solids Introduction

Direct insertion of solid samples into the ICP can be used for metal powders, salts and geological samples. The sample is placed on a wire loop or cup made from

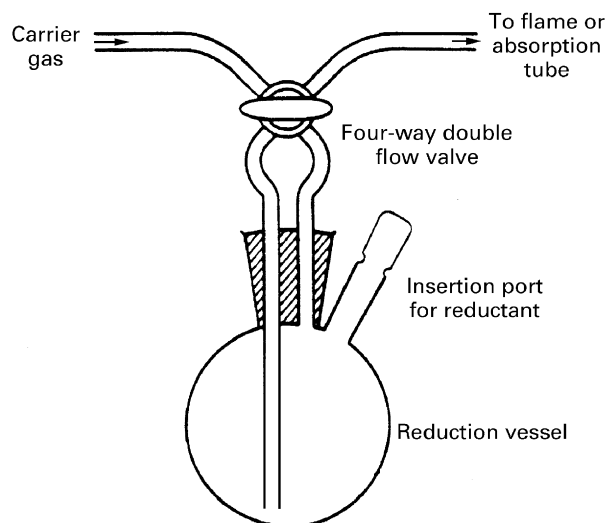


Figure 9 Hydride generation apparatus. Reprint permission from Ingle JD and Crouch SR (1988) *Spectrochemical Analysis*. Englewood Cliffs, NJ: Prentice Hall.

graphite, molybdenum, tantalum or tungsten. The probe is then moved along the axis of the torch and closer to the plasma where drying takes place. At the completion of this stage, the device is propelled rapidly into the core of the plasma and measurements of the analytes can be taken.

Line Selection

The choice of which line to use for a given sample type is a difficult one, as most elements have many lines available for analysis. Not only the intensity of the line but also whether the line is free of spectral interferences from both the plasma and other sample constituents should be considered. Additionally, the nature of the emission, atomic or ionic, should be considered. The emission could originate from an excited neutral atom, which is termed an atomic transition, or an excited ionized form of the element, which is called an ionic transition. While analysis of elements undergoing transitions of the ionic type tend to experience fewer consequences due to changes in the plasma operating conditions, there are elements that produce no ionic lines, such as aluminium and boron. There are very good reference books which list tables of spectral lines and are included in the Further reading section. Often modern instrumentation has sufficiently 'intelligent' software to assist the operator with line selection.

Spectral Interferences and Correction Techniques

A spectrometer with good resolution will help greatly in the separation of adjacent lines from the spectral line of

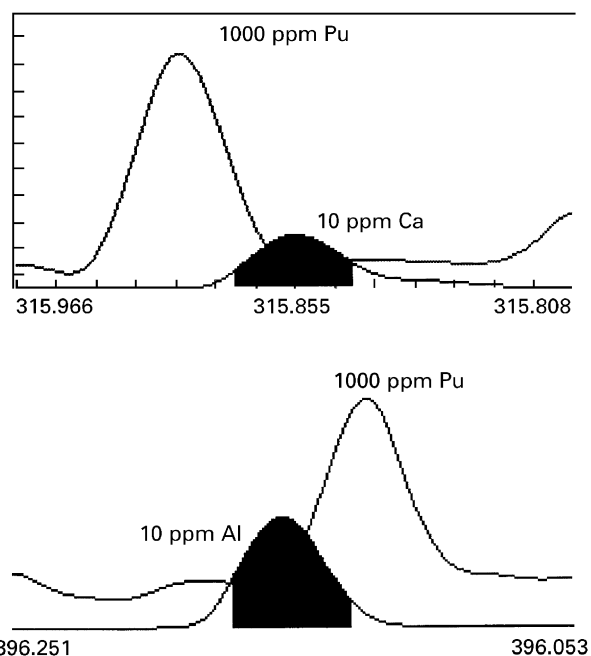


Figure 10 Interelement effects of plutonium on calcium (top) and aluminium (bottom).

interest. The effect of partial overlap can be minimized in some cases with a high-resolution spectrometer, and in other cases, can be overcome using correction techniques.

When the interference is from the plasma emission background, there are background correction options available with most commercial instrumentation. The region adjacent to the line of interest can be monitored and subtracted from the overall intensity of the line. If direct spectral overlap is present and there are no alternative suitable lines, the interelement equivalent concentration (IEC) correction technique can be employed. This is the intensity observed at an analyte wavelength in the presence of 1000 mg l⁻¹ of an interfering species. It is expressed mathematically as

$$\text{IEC} = \left(\frac{I_{\text{init}}}{I_a} \right) \times C_a$$

where the correction is in milligrams of analyte per litre of solution, and I_{init} is the intensity read at the analyte wavelength in the presence of 1000 mg l⁻¹ of the interfering species, I_a is the intensity the instrument will produce for a certain analyte concentration at the analyte wavelength, and C_a is the concentration in mg l⁻¹ used to give I_a . This correction can be applied to all the analytes in a method and some instrument manufacturers' software will automatically perform the necessary corrections. Examples of the effect of 1000 ppm plutonium as the interfering element on calcium and aluminium are shown in Figure 10. This shows the subarrays obtained for separate solutions of plutonium, calcium and

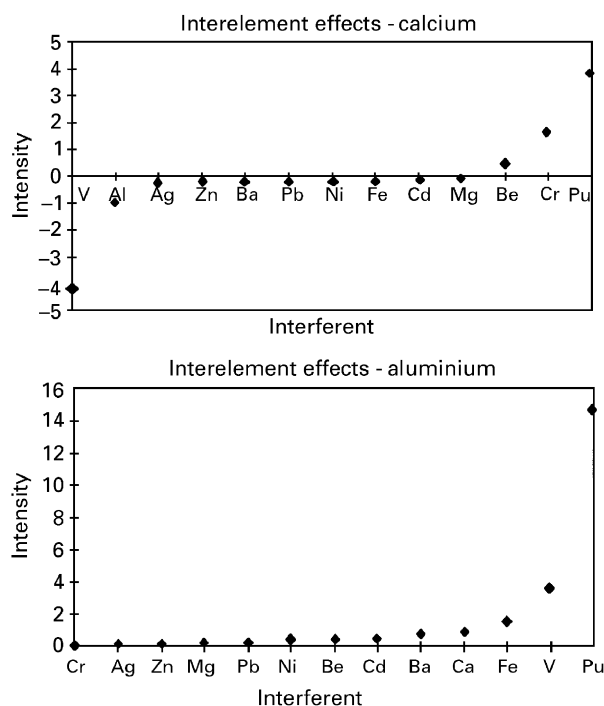


Figure 11 Inter-element equivalent concentration correction factors for several interfering elements on calcium (top) and aluminium (bottom).

aluminium. Graphical representations of interfering elements on calcium and aluminium are shown in [Figure 11](#). These graphs are produced by a program written at Los Alamos National Laboratory by DJ Gerth

and illustrate which interfering elements have the strongest effect on the analytes. The elements with the strongest deviation from the average are those needing the inter-element correction.

See also: Atomic Absorption, Methods and Instrumentation Inductively Coupled Plasma Mass Spectrometry, Methods.

Further Reading

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