

Chemistry Lab Cookbook

ICP Concepts v 210.0

Instrument:

Jobin Yvon Ultra-Ace 2000
 ODP #: 05669
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Website:

<http://www.jyemission.com/>

Software:

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Document Name/Title/Number	Source	Type	Associated Instrument(s)	Associated Measurement(s)
ICP Installation/Setup Binder	Jobin Yvon	hardware	ICP	elemental analysis
ICP Instrument Manuals Binder (Final Control Report; User Manual; Image Navigator User Manual; Sampler AS421 User's Manual; Schematics)	Jobin Yvon	hardware, software	ICP	elemental analysis
ICP Reprints Binder	scientific journals	data	ICP	elemental analysis
ICP Software V5.1 Binder (User Manual)	Jobin Yvon	software	ICP	elemental analysis
ICP Standards Cert./MSDS Binder	misc.	data	ICP	elemental analysis
ICP Technotes, Software Notes, Concepts, Spreadsheets, Etc. Binder	in-house	hardware, software, data, reprints	ICP	elemental analysis
JY Service Manual	Jobin Yvon	hardware	ICP	elemental analysis

CONCEPTS AND METHODOLOGY IN INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY (v.192)

I. PRINCIPLE OF METHOD

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?".

The inductively coupled plasma (ICP) technique is one of the most commonly used techniques to answer that question. This technique measures all of the stable elements in the periodic table-with the exception of gases. It is especially useful at determining trace concentrations of elements in sample.

The ICP technique is based on atomic spectrometry. Most specifically, the **ICP-ES** is an emission spectrometric technique that exploits the fact that excited atoms emit energy at a given wavelength as the electrons return to their ground state. A given element emits energy at specific wavelengths peculiar to its chemical character. Although each element emits at many wavelengths, in ICP-ES it is most common to select a single wavelength (or a very few) for a given element. The intensity of the energy emitted at that wavelength is proportional to the amount (concentration) of that element in the analyzed sample. Thus, by determining which wavelengths are present in a sample, and by determining their intensities, the analyst can quantify the composition of the given sample.

The following sections provides an introduction to some fundamental concepts regarding atomic spectrometry and the analytical techniques based on this field of study. General characteristics of ICP-ES are also discussed.

A. Fundamental Concepts Of Atomic Spectrometry

1. Definitions

Atomic spectrometry is a technique that uses electromagnetic radiation (light) that is absorbed by and/or emitted by charged atoms or ions of a sample. 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 **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 (see Figure 1).

When the electrons of an atom are in the orbitals closest to the nucleus, the atom is in its lowest most stable state, called the **ground state** of an atom. When energy is added to the atom as the result of absorption of electromagnetic radiation or collision with another particle (electron, ion, atom or molecule), the atom can absorb the energy and will be said to be in an **excited state**; i.e, when an atom becomes excited, an electron from the ground state orbital is displaced into an orbital further away from the nucleus and with a higher energy level.

If the energy absorbed by an atom is high enough, an electron can be dissociated completely from the atom, leaving an ion with a net positive charge. This process is called **ionization**. An atom is less stable in its excited state and will thus decay back to a less excited state by losing energy or by **emission** of a massless particle of

electromagnetic radiation, known as **photon**. The number of photons emitted is proportional to the number of atoms in the element under consideration.

The process in which an electron of an atom or ion is transferred at a different level energy is called **energy transition**. The difference in energy between the upper and lower level of an energy transition (whether absorption or emission) defines the wavelength of the radiation that is involved in that transition. Every element will have its own characteristic set of energy thus its own unique set of absorption and emission wavelengths (see Figure 2)

In summary, **atomic absorption spectrometry** is a technique that measures the energy gained by an atom (or ions) as it is passing from a ground state to an excited state while **atomic emission spectrometry** measures the energy lost by an atom (ion) as it is passing from a highly excited state to a lower state of excitation.

2. Analytical Techniques Based on Atomic Spectrometry

In atomic spectrometry techniques most commonly used for trace element analysis, the sample is decomposed by intense heat into a hot cloud of gases (vapor) containing free atoms and ions of the element of interest.

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

In **optical emission spectrometry** (OES), the sample is subjected to temperatures high enough to cause not only dissociation into atoms but to cause significant amount 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 a lower state through emission energy transitions. In OES, the intensity of the light emitted at specific wave lengths is measured and used to determine the concentrations of the elements of interest.

In **atomic fluorescence** spectrometry (AFS), a light source is used to excite atoms only of the element of interest through absorption transitions. When these selectively excited atoms decay, their emission is measured to determine concentration much in the same way as in OES.

In **atomic mass spectrometry**, instead of measuring the absorption, emission or fluorescence of radiation from a high temperature source, mass spectrometry measures the number of singly charged ions from elemental species within a sample. A quadrupole mass spectrometer separates the ions of various elements according to their mass-to-charge ratio in atomic mass spectrometry.

3. Atomization and Excitation Sources

Three types of thermal sources are used in analytical spectrometry to dissociate sample molecule into free atoms: flames, furnaces and electrical plasmas.

Flames and furnaces are hot enough (3000°K-4000°K) to dissociate most types of molecules into free atoms. These two sources can be used to excite many elements for emission spectrometry (especially alkali elements), but absorption will be the preferred method to detect the presence of elements of interest.

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, radical and molecules. Two characteristics of plasmas are that they can conduct electricity and they are affected by a magnetic field. In ICP-OES, the plasma is a gas that has been ionized to a high degree and is electrically neutral. The present state of art in plasma sources for OES is the argon supported inductively coupled plasma (see section below for definition). One of the important reasons for

superiority of the ICP plasma over flames and furnaces is in the high temperature within the plasma (6800°K).

B. General Characteristics of ICP-ES

Routine determination of 70 elements can be made by ICP-OES (ICP-ES in short) at concentration levels below one ppm (mg/L). Figure 3 shows the periodic table of the elements that can be determined by ICP-ES along with their detection limits.

1. Plasma

The inductively coupled plasma used in OES consists of a high temperature discharge generated by flowing a conductive gas (argon) through a magnetic field induced by a coil that surrounds the tubes carrying the gas.

More specifically, argon gas is directed through a torch consisting of three concentric tubes made of quartz (see Figure 4). 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 oscillates within the coil at a rate corresponding to the frequency of the generator. This RF oscillation of the current in the coil causes RF electric and magnetic fields to be set up in the area on top of the torch. The lines of force produced by the magnetic field are directed along the axis of the coil inside the tube and take an elliptical configuration outside it. 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 caught up in the magnetic field and accelerated by them. These high-energy electrons in turn collide with other argon atoms, stripping off more electrons. This collisional ionization of the argon gas continues in chain reaction, breaking down the gas into a plasma consisting of argon atoms, electrons and argon ions (Ar^+). The trajectories of the electrons are slowed by collisions, which heat and ionize other gas atoms and the plasma becomes self-sustained.

The ICP discharge (plasma) appears as a very intense, brilliant white, teardrop-shaped discharge. Figure 5 shows a cross section of the plasma with the nomenclature for the different region of the plasma.

ICP-ES analysis requires a sample to be in solution in order to be introduced into the ICP. These liquids are nebulized into an aerosol, a very fine mist of sample droplets that is carried through the center of the plasma by the inner (or nebulizer) argon flow.

Note: For shipboard analysis, interstitial waters can be thus be analyzed simply, requiring only dilution in most cases. Igneous rocks, sedimentary rocks, and sediments, however, must be dissolved. This can be achieved by a combined acid attack employing HF, HNO₃, and HCl acids with a LiBO₂ flux-fusion technique similar to that used for XRF preparation.

Once the sample is introduced in the plasma, the functions of the plasma are several fold. 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 step involves decomposing the salt particles into a gas of individual molecules (vaporization) that are then dissociated into atoms (atomization) which are then excited and ionized. Figure 6 shows the process that takes place when a single sample droplet is introduced into an ICP plasma. Vaporization and atomization take place mostly in the PHZ zone (see Figure 5), the excitation and ionization occur predominantly in the IRZ and NAZ zones. The NAZ zone is the region of the plasma from which analyte emission is typically measured.

2. Detection of Emission

In ICP-ES, 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 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 spectrometer, which isolates one wavelength of light one at a time, or using a polychromator, which can be used to measure light at several different wavelengths at once.

The actual detection of the light is done using a photosensitive detector such as a photo-multiplier tube (PMT).

3. Extraction of Information

Qualitative analysis involves a search for the elements present in an unknown sample. Such analysis involves a search for the elements' s characteristics spectral lines (wavelengths). If two or more elements show emission at the same wavelength or so close together that separation is impossible, it is necessary to use at least two well known wavelengths to show their presence in the sample.

Quantitative analysis associates the emitted energy with the number of atoms in the sample. Solutions with known concentrations of the element of interest (standards) are introduced in the ICP and the intensity of the characteristic emission for each element in the standard is measured. These intensities are plotted against the concentrations of the standards to form a calibration curve. Sample concentrations for one element will be determined by checking that element intensity in sample against that element's calibration curve.

One advantage of ICP-ES spectrometry technique is that in most cases these calibration curves will be linear over several orders of concentration. It is usually necessary to measure only one standard and a blank to calibrate the ICP. A first order equation is determined as follows:

concentration = a X intensity + b. If there is sufficient number of standards (minimum 3), a curve of the second order can be calculated where concentration = aX (intensity)² + bX intensity + c.

The standards are samples whose matrix is close to that of the samples to be analyzed and the concentrations in elements to be analyzed are known. The standards can be of multi-element type. All the concentrations of the element to be analyzed from unknown samples should be within the concentration range of the standards used.

4. Performance Characteristics

Detection limit (LDO) is regarded as the lowest concentration at which the analyst can be certain that an element is present in the sample. In ICP-ES, most elements analyzed have LDOs in the ppb (mg/L) range. For accurate quantitation (+2%), the elements' concentrations should be greater than 100 times the detection limit.

The upper limit of linear calibration is usually 10⁴ to 10⁶ times the detection limit for a particular emission line. The range of concentrations from the detection limit to this upper limit is known as the linear dynamic range (LDR) of the emission line.

Advantages of ICP-ES over other atomic spectrometry techniques include:

- multi-element analysis capability;
- linearity of calibration curve over several order of concentrations;
- broad LDR (i.e, ability to work with concentrations running from ppb to % without extra dilutions or changes in analytical conditions);

fewer interferences (only spectral interferences that can be controlled, see Methodology section).

C. Components of ICP-ES (JY 2000 ICP)

A typical ICP spectrometer will include four major components (Figure 7)

a sample introduction system to transport samples into the plasma ;
an electrical generator providing energy for the plasma;
an optical system which analyzes the spectrum emitted by the plasma; and
a signal processing system for making qualitative and quantitative analyses using the emitted radiation.

The following paragraphs will focus mostly on the first three components.

1. Sample Introduction and Torch Assembly

The sample introduction system on the ICP-ES consists of an autosampler, peristaltic pump, Teflon tubing, nebulizer (creates aerosol), spray chamber (sorts droplets) and a removable torch (carries aerosol into the plasma).

Samples are introduced into the plasma in the form of liquid or fine solid particles in suspension in a liquid. Particle diameter should not exceed approximately 10 microns. The fluid sample is pumped into the nebulizer via a peristaltic pump. The nebulizer generates an aerosol mist, and injects humidified argon gas into the nebulizer along with the sample. This mist accumulates in the spray chamber where the largest mist particles settle out as waste and the finest particles are subsequently injected into the torch assembly. Approximately 1% of the total solution is eventually taken into the torch as a mist, with the remainder pumped away as waste.

1.1 Peristaltic Pump

Peristaltic pumps utilize a series of rollers that push the sample solution through the teflon tubes. The pump itself does not come in contact with the solution, only the tubing. The peristaltic pump serves to stabilize flow of the solution regardless of its viscosity. The pump tubing is one of the part of an ICP system that usually requires frequent replacement (check daily). Failure to replace worn tube can result in poor instrument performance.

1.2 Nebulizer

Nebulizers are devices that convert a liquid into an aerosol of very fine droplets (mist) that can be transported to the plasma.

Two major types of nebulizers exist: pneumatic and ultrasonic. The choice in using one over the other depends on the matrix being analyzed.

The most commonly used type of nebulizers is the pneumatic nebulizer with an efficiency close to 5%. The type of pneumatic nebulizer most commonly used is the **concentric nebulizer** (commonly referred to as a Meinhard nebulizer which is used mostly for aqueous solutions). A typical concentric nebulizer is shown in Figure 8. In this nebulizer, the solution is introduced through a capillary tube to a low-pressure region created by argon flowing rapidly past the end of the capillary. The low-pressure and high speed gas combine to break up the solution into an aerosol. Because of the small orifices, Meinhard and other concentric nebulizers provide excellent stability and sensitivity (signal-to-noise ratios), although they are more prone to clogging.

Note: Wide orifice "Type C" concentric nebulizers work well with both rocks and sediments as well as interstitial waters.

A second type of pneumatic nebulizer is the **cross-flow nebulizer** shown in Figure 9. Here a high speed stream of argon gas is directed perpendicular to the tip of the capillary tube (in contrast to the concentric where gas is parallel to capillary). The solution is either drawn up through the capillary by the low pressure region created by the high speed gas or forced up with a pump. In either case, contact between the high-speed gas and the liquid stream causes the liquid to break into an aerosol. Cross-flow nebulizers are usually not as efficient as concentric nebulizers at creating small droplets. However, the large diameter capillary and longer distance between liquid and gas injectors minimize clogging.

The third type of pneumatic nebulizer is the **V-groove nebulizer** (a variation of the Babbington nebulizer) as shown in Figure 10. In this nebulizer, the sample flows down a groove which has a small hole in the center for the nebulizing gas. High speed gas 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. The V-groove nebulizer allows for the analysis of solutions with high salt and particulate concentrations (for example, a concentration of salt greater than 10 g/L). It is also used for solutions in a hydrofluoric acid matrix, organic solutions, and suspensions in solution. This nebulizer requires a slightly higher sample uptake speed (controlled through the peristaltic pump) than a concentric nebulizer, and thus consumes more analyte, but the flexibility to easily analyze different TDS (total dissolved solid) solutions makes this nebulizer particularly well suited for high TDS operation. Note, however, that signal stability is significantly poorer for V-groove nebulizers, and thus they should only be used in exceptional circumstances.

Note: Testing of "Type C" concentrics and V-grooves during Leg 187 and at Boston University documented that the concentric nebulization scheme provided a greater signal, better stability, and less noise for the analysis of rocks, sediments, and interstitial waters, at the dilution factors suggested for routine operation (4000x dilution for rocks, 10x dilution for pore waters).

In the **ultrasonic nebulizers**, the liquid sample is pumped onto an oscillating piezo electric transducer. The oscillations break the sample into a fine aerosol, so aerosol formation is independent of nebulizer gas flow. The efficiency of this type of nebulizer is at least 10-fold greater than pneumatic nebulizers for working at very low detection limits. The higher efficiency of the ultrasonic nebulizer increases the water load to the ICP, so a desolvation unit is added after the nebulizer (Figure 10). However, this nebulizer is still susceptible to matrix effects, high solids loading and is not HF resistant.

Conditions of various types of use of nebulizers are shown in Table 1. Notice that to form an aerosol, three parameters must be adjusted or verified: argon pressure at the inlet to the nebulizer, nebulizing gas flow, and sample rate flow.

For the analysis of aqueous solutions with high concentrations of salts, an **argon humidifier** can be installed ahead of the argon inlet in the nebulizer. The humidification of the argon gas used for the nebulizer is important when analyzing samples with high dissolved solids, as is often the case with analysis of ODP rocks, sediments, and interstitial waters. It is used to reduce the danger of clogging of the nebulizer. It should not be used for organic solutions. The humidification occurs in the argon humidifier by bubbling argon through deionized water prior to its expulsion in the nebulizer.

1.3 Spray Chamber

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 (condensation chamber), where large droplets are eliminated by gravity, is placed between the nebulizer and the torch.

There are two types of spray chamber available: Scott and Cyclonic (Figure 11). Liquid that is not used by the

torch is drained off or pumped out. About 1-5% of the total solution is introduced in the torch as a mist, the remaining 95-99% is pumped away as waste.

1.4 Torch Assembly

From the spray chamber, the fine aerosol mist is injected vertically up the length of the torch assembly into the plasma where it is desolvated, vaporized, atomized, and excited and/or ionized by the plasma. The torch assembly consists of the torch body, inner and outer tube, alumina injector, and aerosol sheath (Figure 12).

The torch (which is fully removable in the case of the JY2000) is made up of three concentric tubes for argon flow and aerosol injection:

- an external (**outer**) quartz **tube**;
- an intermediate (**inner**) quartz **tube**; and
- a **alumina central injector tube**.

These three tubes delimit three channels for argon flow.

The external channel is defined by the spacing between the outer and inner tubes. This channel is kept narrow so that gas introduced between them emerges at high velocity. The external channel is also designed to make the gas spiral tangentially around the chamber as it proceeds upwards. One of the function of this gas is to keep the quartz walls of the torch cool. For axial plasma, this tube is 20mm longer in order to extend the length of the plasma. The outer or **plasma flow** is usually 7 to 15 liters per mn (14L/mn for JY2000);

The intermediate channel is defined by the spacing between the inner and injector tubes. It sends gas directly (axial flow) under the plasma to lift the plasma tip away from the injector. This **auxiliary flow** is usually about one liter per mn and is used mostly with organic solution (not used on JY2000 for our purpose):

The central channel is defined by the central tube or injector. This argon flow, that carries the sample in the form of an aerosol, is injected into the plasma through the injector. This flow is called **nebulizer** or inner **flow**.

The sheath is a device installed on the JY2000 only. It is used to envelop the aerosol with argon gas. The use of this additional gas has two advantages:

- it reduces problems of memory effect, pollution and crystallization in the injector;
- the **sheath gas flow** can be varied (without affecting the other parameters) which causes a variation in the time the sample spends in the plasma. This makes it possible to analyze alkaline elements (such as Na, Li, and K) with increased sensitivity.

The torch is assembled by inserting successively into the torch body (Figure 12):

- the sheath;
- the injector;
- the teflon centering piece;
- the inner tube;
- the outer tube.

Before assembling, verify the O-rings, lightly grease the bases of the outer and inner tubes and insert these tubes gradually while turning them. Push them all the way to their stops. Once assembly is completed, verify that the top of the injector tube is 1mm below the top of the inner tube.

Figure 13 shows the proper torch alignment with respect to the induction coil and optical axis.

2. Radio Frequency Generator

The function of the RF generator is to deliver power required to obtain and maintain the plasma, portions of which are as hot as 10,000°K. 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 coils is made of copper tubing and is cooled by water during operation.

The JY2000 generator is a solid state RF generator. It is a “crystal-controlled” generator where the frequency is produced by a quartz and amplified with CMOS amplifier. The inductor is in a secondary circuit. Any variation in the load, that is in the type of solution inserted in the plasma, is compensated for by a modification in the coupling between the primary lines and the lines of the secondary circuit. The frequency is selected at 40.68MHz, which is a high frequency thus providing a weak background and excellent limits of detection.

3. Collection and Detection of Emission

The emission radiation from the plasma (NAZ zone) can be viewed either radially (as in JY 2000) or axially by an optical channel. Light emitted from the NAZ region is focused through a lens, and passes through an entrance slit into a spectrometer.

There are two types of spectrometers used in ICP-ES analysis: sequential (monochromator) and simultaneous (polychromator).

The JY2000 is a sequential device. This means that the diffraction grating in the spectrometer acts analogously to a prism that breaks visible light into its resultant colors. If a detector (photomultiplier tube) is fixed in space at the far end of the spectrometer, rotating the grating will sequentially move each wavelength across the detector. The computer control ensures that the detector is coordinated with the grating, so that the intensity at the detector at a given time is correlated with the wavelength being diffracted by the grating. The user programs into the computer which wavelengths s/he wishes to analyze; the grating sequentially moves to those wavelengths and determines the intensity at each wavelength to provide a quantitative analysis.

3.1 Optical System

The emission radiation from the plasma (NAZ) is sampled for spectrometric measurement. The plasma can either be observed from the side of the plasma operating in a vertical orientation as shown in Figure 14a. (referred to as radial or **side-on viewing** of the ICP) or the plasma can be rotated to a horizontal position and the NAZ is observed from the end of the plasma as illustrated in Figure 14b. (referred to as axial or **end-on viewing** of the ICP). Recently, instruments that combine both radial and axial viewing, called dual viewing, have been introduced.

On the JY 2000, the plasma has a side-on viewing configuration.

No matter the type of configuration, the radiation is usually collected by a focusing optic (convex lens in the case of JY2000). The optic focuses the image of the plasma onto the entrance slit of the wavelength dispersing device or spectrometer (monochromator or/and polychromator).

The **spectrometer** is a device used to separate, isolate and measure light according to the wavelength. There are two types of spectrometers used in ICP-ES analysis: sequential (monochromator) and simultaneous (polychromator).

Monochromators are used in multi-element analyses by scanning rapidly or sequentially from one emission line to another. They are two types of monochromators: Czerny-Turner and Ebert as shown in Figure 15.

The JY2000 is a sequential (monochromator) device of the Czerny-Turner type.

A Czerny-Turner monochromator usually comprises:

- a input slit controlled by computer through which the light emitted from the plasma enters;
- a collimating mirror which sends light to the grating;
- a plane grating used for light diffraction; and
- a mirror which transmits light to the output slit.

The diffraction grating is always the core of the spectrometer. It is simply a mirror (glass support) covered with a photosensitive layer with a large number of etched parallel lines (between 1800 and 4320 lines/mm for the JY2000). The purpose of the grating is to break down the white light into a number of different wavelengths. On the JY configuration, the grating rotates about its axis.

Note: Physical dispersion of the different wavelengths by diffraction grating is by far the most common devices used. Other devices include prisms, filters, interferometers and echelle grating.

Polychromators are used for simultaneous multi-element analyses. The most popular design is the Paschen-Runge design. This spectrometer consists of an entrance slit, a concave fixed grating (3000 to 3600 grooves/mm), and multiple exit slits, all on the periphery of what is known as the Rowland circle (Figure 16). In this type of configuration, there is an exit slit for each analytical wavelength. There are as many slits as there are elements to be analyzed. Usually the number of output slits for a JY instrument are limited to 47 because of bulkiness.

Polychromator- and monochromator-based ICP-ES instruments each have their own relative advantages and disadvantages.

With polychromators, 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. Since the spectral line array for polychromator is fixed, spectral interferences corrections may be applied to the analyte only if a spectral line for the interfering element line is not included.

The major advantage of the monochromator-based system is their spectral flexibility, i.e the ability to access, at any time, any wavelength within the range of the monochromator. Because elements are sequentially addressed, monochromators require large amounts of sample. Using standard spectroscopic techniques (e.g., background corrections), sequential ICP-ES provides for extremely flexible and rapid analysis of a number of chemical elements.

Note: The spectrometer is flushed with nitrogen gas to improve the detection limits of elements with emission wavelengths that are severely compromised by interference with air (e.g. P). This nitrogen flush, which is constantly maintained in the instrument regardless of what element is being analyzed, also protects the optics from the corrosive aspects of the atmosphere, which are particularly acute at sea.

3.2 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-ES is the photomultiplier tube or PMT (Figure 17).

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 multiplicative effect along the way. Typical PMTs contain 9 to 10 dynode stages. The final step is the collection of the secondary electrons from the last dynode by the anode. The electrical current measured at the anode is then used as a relative measure of the intensity of the radiation reaching the PMT.

On the JY2000, the signal from the PMT is treated by the **Spectralink** which serves as interface between the spectrometer and the computer. The Spectralink comprises of 6 different PCBs including the Low and High voltage PCBs (power PMT with low and high voltages), Interface PCB (allows communication between Spectralink and computer via RS32), MDR PCB (powers grating motor), PIO PCB (controls accessories such as autosampler), and Acquisition PCB (acquires signal from the PMT).

II. ICP-ES METHODOLOGY

There are several features common to the ICP-ES methodology used in an analysis: sample preparation, sample introduction, instrument calibration, and element or wavelength selection. Once decisions have been made regarding these steps, the analyst will spend a lot of time refining the method by optimizing the operating parameters and correcting for interferences. These latter subjects will be the focus of the next paragraphs.

A. Operating Parameters

The conditions used for the operation of the ICP and the measurement of emission are important for any ICP methodology. For routine analysis, the standard operating conditions as suggested by the manufacturer are usually sufficient. Virtually every ICP-ES instrument has two sets of standard operating conditions—one for aqueous solutions and one for organic solutions. The differences in operating conditions between these two types of solutions are dictated by the sample matrix rather than the elements to be determined in the samples. Organic solutions require analysis at increased power levels simply to sustain the plasma during analysis.

Table 2 shows the typical standard operating conditions for the JY2000.

Some analysis, however, 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-ES are determined by a number of variable parameters. The most common parameters that are varied are the mode of analysis (acquisition mode), PMT voltage or gain, argon flow rates, and RF power. All operating parameters will be discussed in reference to the JY2000.

1. Acquisition Parameters

The operator will define the following acquisition parameters:

- The acquisition mode (integration mode);
- The integration time (spent on each points (sec));
- The entrance and exit slit of the monochromator (nm);
- The points used for calculation;
- The increment between two points of measurement (nm);
- The mode of intensity estimation (gain).

1. 1 Acquisition Mode and Slit Width

Two types of acquisition mode (mode of analysis) are most commonly used with the JY200: the "maximum" mode and the "gaussian" mode. For a simultaneous instrument, you have only the "maximum" mode.

With the "**Gaussian**" mode (mode 2 for version 4 of software): the software makes a scan around the theoretical position of the peak. It determines a gaussian curve corresponding to these points and then integrates to determine the area under the curve. The "gaussian" mode can compensate for a small variation in peak position. The integration time for each point is short because the number of points is high. Nine points of measurement are usually taken and five of these are used for calculating the gaussian curve.

With the **Maximum** mode (mode 2 for V4) the software goes directly on the top of the peak and makes the acquisition on one or several points (usually 3 points). Because of the small number of points, the integration time can be high, even for a total short analysis time. If the number of points is greater than one, the mean value of the chosen points is made.

The "**Mean**" mode (mode 1 for v4) is often also used. It measures intensities at a variable number of points (3-11) across a peak and then averages the intensities of a subset (1-9) of those points with the largest intensities. For example, Mode 1 will average the intensities of the three highest contiguous "points" within a set window of up to 11 preset nanometer intervals across a peak.

Entry

Entry

Exit

Profile peak

For a sequential instrument, the choice of the acquisition mode depends on the width of the slits (entrance and exit slit of the monochromator) and on the expected concentration of the element. This choice has to be done by element in order to optimize the analysis conditions. If the slits are symmetric, the peak profile is sharp. If the slits are di-symmetric, the peak has a plateau on its top.

Symmetric Slits

Di-symmetric slits

The "maximum" mode is generally associated with dis-symmetric slits, because even with a slight variation in position of the peak, the measurement is done on the top of the peak. The "gaussian" mode is associated with symmetric slits, because in that case the shape of the peak is gaussian.

After an interference study, the possible widths of the slits are defined by the entrance/exit slits typically 20 x 15 and 20 x 80 for a monochromator of 1 m focal length or 20 x 25 and 20 x 50 for a 0.64 m focal length monochromator (JY2000)

The resolution of the monochromator is defined by the widest slit used. The narrower the slit the better is the resolution and the sensitivity. So for measuring low concentrations, it is better to use narrow slits.

For example for the JY2000, you can use slits 20 x 15 for the determination of trace elements and slits 20 x 80 for determination of major elements if there are no interferences.

1. 2 Integration Times

A important parameter to also select is the integration time, or the time spent measuring the emission intensity at each wavelength. While the precision of an analysis can be improved by increasing the integration time, there is also a trade-off in the speed of an analysis when a longer integration time is used. A longer integration time could be used when the signal for an element is expected to be weak while a shorter time may be used for an element with a strong signal.

JY recommends that for very low concentrations, narrow slits and high integration times are required. With long integration times only the "maximum" mode of measurement is practical with repeat peak searches.

The following table summarizes standard conditions of operation (to acquisition mode, slit width, integration times, increments between two points) with the JY 200 for different sample concentrations:

Concentration	Analysis mode	Integration time (s)	Incr. between 2pts(nm)	Slits
> 20 mg/l	Max (1/1)	2	0,003 for $\lambda < 310$ nm 0,004 for $\lambda > 310$ nm	20/80
	Mean (3/3)	0,5	0,005 for Na, Li, K	20/80
			0,003 for $\lambda < 310$ nm 0,004 for $\lambda > 310$ nm 0,005 for Na, Li, K	20/15
0,5 < Conc < 20	Gauss (9/5)	0,3	0,003 for $\lambda < 310$ nm 0,004 for $\lambda > 310$ nm 0,005 for Na, Li, K	20/15
			0,003 for $\lambda < 310$ nm 0,004 for $\lambda > 310$ nm 0,005 for Na, Li, K	20/15
0,1 < Conc < 0,5	Max (5/1)	0,5	0,003 for $\lambda < 310$ nm 0,004 for $\lambda > 310$ nm 0,005 for Na, Li, K	20/15
< 0,1	Max (5/1)	1	0,003 for $\lambda < 310$ nm 0,004 for $\lambda > 310$ nm 0,005 for Na, Li, K	20/15
™ LQ	Mean (3/3)	2	0,002 for $\lambda < 310$ nm 0,003 for $\lambda > 310$ nm 0,004 for Na, Li, K	20/15

With
Conc: concentration of the element
LQ: limit of quantification
Max: Mode maximum
Mean: Mode mean
Gauss: Mode gaussian

2. PMT High Voltage and Gain

PMT High Voltage (HV) affects the stability and sensitivity of the results and it is important to adjust it. The PMT voltage and gain are a function of the expected intensity of the emission to be measured. A high voltage/gain is used for measuring weak emission while a lower voltage/gain is used for measuring strong intensities. However, too high the HV and the PMT stability will suffer. On the version 4 of JY software, the last number in the H.V. Field represents the gain. If the HV number finishes with 1, the gain is 1. If the HV number finishes with 2, the gain is 2. For all other numbers, the gain is 3. For example, 625 V corresponds to 620 volts at gain 3.

With the version 5 of the JY software, the gain is either 1, 10, or 100. For example, for an intensity of 123 counts in gain 1, for one second of integration, electronically this is 1230 in gain 10, and 12300 in gain 100. The software will normalize the value and displays 12300 whatever the gain. The normalized value is the one in gain 100 for one-second-integration time.

3. Argon Flow Rate

Nebulizer argon flow 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 (difficult to ionize), a long residence time would be desired. Thus a lower nebulizer 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. On the other hand, for elements such as sodium and potassium that emit strong atomic lines but are easily ionized, a faster flow rate might be used so that the atoms are not ionized before they can emit the desired radiation.

4. RF Power

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 is applied to the plasma, the hotter it gets. For analyte species that require more energy for excitation and ionization, a higher power would provide greater sensitivities. For an easily excited analyte, such as sodium, a lower power would increase sensitivity.

B. ICP-ES Interferences

For 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 the analyte in a calibration solution. The interferences we know today in ICP-ES are mostly 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.

1. Spectral Interferences

Spectral interferences are due to;

the continuous background emitted by the plasma that becomes superimposed on the radiation from the line being studied;
radiation from another atomic line superimposed on the analytical line;
the superimposition of molecular bands from argon lines on the analytical line; and
the background produced by the matrix.

1.1 Plasma Interferences

The continuous background emitted by the plasma is an emission of constant intensity at least within the wavelength interval containing the analytical line. It is easy to compensate for by subtracting its measured value in the neighborhood of the analytical line from the line's maximum peak value.

1.2 Spectral Overlap

The problem arises when the lines coming from different elements are of exactly the same wavelength or so close to one another that the spectrometers are unable to differentiate between them. If the distance between lines is too small, analytical results will be accurate only if the analyst has previously made use of an **inter-element correction (IEC)** program to offset the disturbance.

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. Unless the difference in the wavelengths of the overlapping lines is less than about 0.002nm, interfering element correction is generally not useful for correction of direct spectral overlaps when using a sequential ICP-ES instrument that scans over the analyte emission line to locate the peak.

1.3 Argon Interferences

The plasma emits spectra or bands from the NO, OH and NH radicals between 200 and 350 nm. In addition, the plasma also emits argon lines that in some cases may be superimposed on the atomic lines from the element being analyzed. Consequently, the background will not be uniform at all wavelengths. In some cases corrections can be made.

1.4 Matrix Interferences

An important concept related to sample preparation and interference correction is that of matrix matching. **Matrix matching** involves preparing solutions 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. While matrix matching involves matching the solvents, it also involves matching the concentrations of acids and other major solutes.

The matrix interferences most commonly encountered in ES results from high concentration of dissolved solids in the sample solutions. These interferences can be corrected by the software.

In case where the standard and sample matrices are quite different or cannot be matched and an interference occurs as a result, internal standards can be used. In this technique, an element, known as the **internal standard**, is added to the standards, blanks and samples. The emission signal from the internal standard is then used to correct mathematically for differences in sample introduction efficiencies.

2. Chemical and EIEs Interferences

In most cases, chemical interferences are not observed in ICP-ES. **Chemical interferences** arise when some

element or molecule in the sample causes a particular analyte to vaporize either more or less quickly than the analyte vaporizes in a solution without the interferant (e.g. effect of aluminum on calcium). 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.

Another type of interferences occasionally encountered in ICP -ES 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 are Li, Na, K, Ca and Fe. In samples that contained high concentrations of EIEs, suppression or enhancement of emission signals, depending on the analyte species, is possible.

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