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Review Article

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Inductively coupled plasma emission spectroscopy an overview

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ABSTRACT

Inductively coupled plasma/optical emission spectrometry (ICP/OES) is a powerful tool for the determination of metals in a variety of different sample matrices. With this technique, liquid samples are injected in to a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried vaporized, and energized through collisional excitation at high temperature. The atomic emission emanating from the plasma is viewed in either a radial or axial configuration, collected with a lens or mirror, and imaged on to the entrance slit of a wavelength selection device. Single element measurements can be performed cost effectively with a simple monochromator /photo multiplier tube (PMT) combination, and simultaneous multi element determinations are performed for up to 70 elements with the combination of a polychromator and an array detector. The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regards to sample throughput and sensitivity.

Keywords: ICPS, RF Power, Interference

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CONTENTS

1. Introduction787
2. Principle.787
3. Instrumentation.787
4. Applications.790
5. Summary and conclusion790
6. References790

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1. Introduction

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), and is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. Liquid and gas samples may be injected directly into the instrument, while solid samples require extraction or acid digestion so that the analytes will be present in a solution. The sample solution is converted to an aerosol and directed into the central channel of the plasma. At its core the inductively coupled plasma (ICP) sustains a

2. Principle

Inductively coupled plasma/optical emission spectrometry (ICP/OES) is a powerful tool for the determination of metals in a variety of different sample matrices. With this technique, liquid samples are injected in to a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried vaporized, and energized through collisional excitation at high temperature. The atomic emission emanating from the plasma is viewed in either a radial or axial configuration,

3. Instrumentation

The instrumentation of inductively coupled plasma/optical emission spectrometry are:

A. Torch:

Torch is usually an assembly of three concentric fused-silica tubes. These are frequently referred to as the outer, intermediate, and inner gas tubes. The diameter of the outer tube ranges from 9 to 27 mm. A water-cooled, two- or three-turn copper coil, called the load coil, surrounds the top section of the torch, and is connected to a RF generator. The outer argon flow (10 – 15 L min sustains the high

B. Nebulizer:

There are numerous types of nebulizers for a variety of specific applications, the three most commonly types are:

a. Pneumatic:

Pneumatic nebulizers are two types

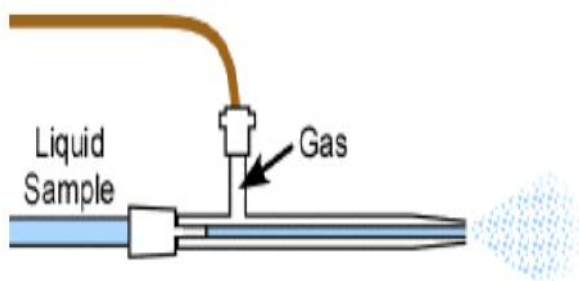


Figure 1: Pneumatic concentric nebulizer

temperature of approximately 10 000 K, so the aerosol is quickly vaporized. Analyte elements are liberated as free atoms in the gaseous state. Further collisional excitation within the plasma imparts additional energy to the atoms, promoting them to excited states. Sufficient energy is often available to convert the atoms to ions and subsequently promote the ions to excited states. Both the atomic and ionic excited state species may then relax to the ground state via the emission of a photon. These photons have characteristic energies that are determined by the quantized energy level structure for the atoms or ions. Thus the wavelength of the photons can be used to identify the elements from which they originated. The total number of photons is directly proportional to the concentration of the originating element in the sample.

collected with a lens or mirror, and imaged on to the entrance slit of a wavelength selection device. Single element measurements can be performed cost effectively with a simple monochromator / photo multiplier tube (PMT) combination, and simultaneous multi element determinations are performed for up to 70 elements with the combination of a polychromator and an array detector. The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regards to sample throughput and sensitivity.

temperature plasma, and positions the plasma relative to the outer walls and the induction coil, preventing the walls from melting and facilitating the observation of emission signals. The plasma under these conditions has an annular shape. The sample aerosol carried by the inner argon flow (0.5–1.5Lmin enters the central channel of the plasma and helps to sustain the shape. The intermediate argon flow (0 – 1.5 L min is optional and has the function of lifting the plasma slightly and diluting the inner gas flow in the presence of organic solvents.

Pneumatic concentric nebulizer is used for the low sample concentration dissolving solids.

Pneumatic Babington nebulizer is used for higher suspended solids and dissolved solids Sample.

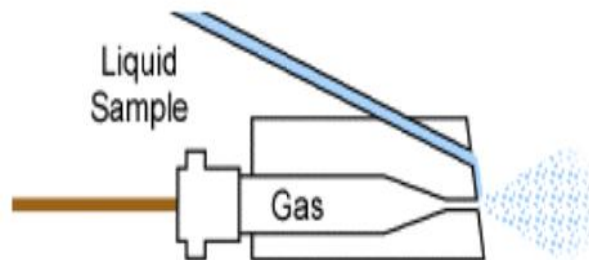


Figure 2: Pneumatic Babington nebulizer

B. Ultrasonic nebulizer:

Ultrasonic nebulizers are used to provide more sample delivery to the plasma and thus improve detection limits. An ultrasonic generator surface, usually a piezoelectric crystal that rapidly vibrates to generate sonic energy is used to create extremely fine droplets that, at low flow rates, are completely transferred to the plasma

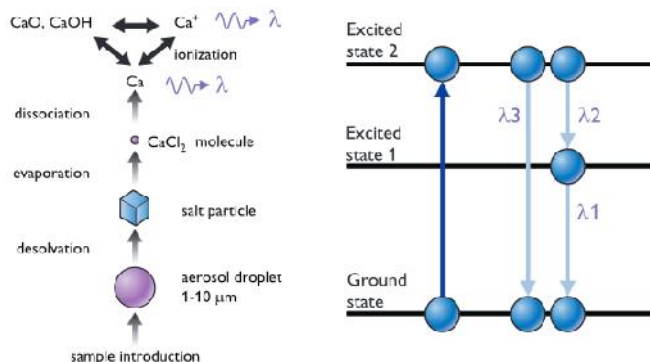


Figure 3: Sample introduction process

C. Hydride generation:

HG is a very effective sample introduction technique for some elements. These elements include arsenic, bismuth, germanium, lead, antimony, selenium, tin, and tellurium. In this method, the sample in diluted acid solution is mixed with a reducing agent.

D. Electro thermal vaporization:

ETV has also been used to solve problems associated with pneumatic nebulization. Graphite furnaces or other electro thermal devices, such as carbon rods, carbon cups, graphite boats, graphite tubes, tungsten wire, and other metal filaments, have been used in research laboratories to electro thermally vaporize a liquid or solid sample for introduction into the ICP. A small portion of the sample is then vaporized by the device through the application of a high current. An optional "ash" step may be used to remove some of the matrix prior to the analyte vaporization step. The resulting dense cloud of the analyte vapor is then efficiently swept into the center of the plasma by a flow of argon gas. A commercial graphite furnace designed for AAS is most frequently used in ETV/ICP/OES. The major advantage of ETV as a means of sample introduction is that the transportation efficiency is dramatically improved over a pneumatic nebulizer, from less than 5% to over 60%.

E. Chromatographic couplers: The combination of the separation power of chromatography and the detection power of atomic emission spectroscopy results in many advantages. One of the primary advantages of chromatography over conventional sample introduction is the ability to obtain speciation information. When used as a detector for chromatographic methods, the ICP offers good sensitivity, wide LDR and multi element detection capability. The multi element capability of ICP, in turn, enhances the performance of chromatographic methods. Both gas chromatography (GC) and high-performance liquid chromatography (HPLC) can be coupled with ICP/OES.

F. Torch Configuration:

C. Grid nebulizer:

Grid nebulizers create a fine mist by placing a grid in front of the argon flow. The liquid sample is allowed to flow down the grid and as argon passes through the grid it creates fine droplets.

The atomic emission from the NAZ, as shown in Figure 1, is sampled for spectrometric measurements. Two configurations may be employed for observing emission from the ICP. One is referred to as a radial or side-on viewing of the plasma and the other is known as an axial or end-on viewing of the plasma. A third viewing mode is the combination of these two basic modes, and is known as dual view. These are all commercially available, and each of them has advantages and disadvantages.

Radial View:

The radial view is the classical operation mode for ICP/OES. With radial viewing, the plasma is operated in a vertical orientation, and the analytical zone is observed from the side of the plasma. Radial viewing constrains the observation volume in the NAZ, and thus limits the effect of potential spectral and background interferences.

Axial view:

With the axial view, the plasma is rotated to a horizontal position and the NAZ of the ICP is observed from the end of the plasma. The axial view provides better LOD than radial view. This may be attributed to the longer viewing path available down the axis of the plasma. Thus, a better sensitivity and a 5- to 10- fold improvement in the LOD can be achieved. The disadvantages of the axial view include the increased potential for spectral interference and matrix-induced interferences. Moreover, self-absorption effects can be quite severe because the observations are made through much cooler tail plume of the plasma. These effects can be significantly reduced by use of a shear gas. The shear gas displaces the tail plume from the optical path, and thus reduces the self-absorption. Spectral interferences may be either corrected or minimized by improving spectral resolution, using an alternate analytical line with less or no interference.

Dual view:

In cases of very complicated sample matrices having a wide range of elemental concentrations, the axial view may be inappropriate. Recent commercial instruments combine the

axial view and radial view configurations into a single unit, known as dual view. This dual view system allows the user to optimize the appropriate configuration for the type of sample without the expense two separate systems.

H. detection of emission:

Three broad categories of detection are available for analyzing the emitted photons: sequential, simultaneous multi channel and Fourier transform systems. In the first two, all wavelengths enter a monochromator where they are dispersed by prisms and/or grating monochromators and are then transmitted to the detector (most commonly the PMT presented in Animation 2.4, or a CCD In Fourier transform systems, no slits or monochromators are required, and this creates better detector limits because more intense radiation reaches the detector. Fourier transform systems also have higher spectral resolution (and thus have fewer spectral interferences) and can simultaneously monitor all wavelengths for longer times. This text will only cover sequential and simultaneous multichannel systems that use monochromators because Fourier transform systems extend past the basic ICP instrumentation goal of this E text book and are considered higher end systems. The first ICPAES systems used a sequential monochromator to separate the analyte emitted photons by wavelength before detecting

them with a single detector. This approach is analogous to the FAES system where only one element could be analyzed at a time. In a sequential system, if a sample needed to be analyzed for multiple elements, the grating system was rotated to direct the appropriate wavelength to the exit slit of the monochromator and into a PMT. While ICP AES provided superior detection limits compared to FAES instruments, it was just as slow and labor intensive as FAES. Simultaneous multi channel systems rapidly became economical as component production costs decreased and as labor costs have increased with time. In these systems, multiple elements can be detected at the same time using one of two designs. One way is to use a standard grating monochromator that separates the photons based on wavelength and directs the photons of interest to specific exit slits. Then, a single detector was rapidly moved from one slit to the other to analyze photons of various wavelengths. This type of system is shown another way to accomplish multiple element detection is by placing an individual detector, again usually a PMT, at each exit slit. Such a system, the Rowland circle here as The Rowland design increases the upfront cost of an instrument and the running cost as PMT are replaced but this design significantly decreases the analysis time.

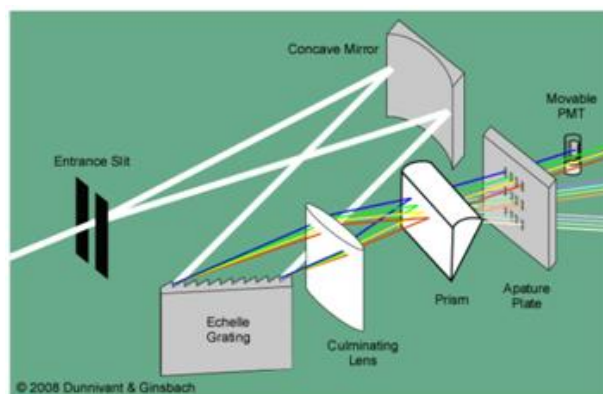


Figure 3: Detector of ICP-AES

I. Interference

ICP systems greatly reduce the number of interferences over those created in flame based systems. Nebulizer, chemical, ionization, and spectral interferences are all present in ICP systems, but spectral interferences are most prominent. Nebulizer interferences (also known as matrix effects) can arise from physical and chemical differences between reference standards and samples, or between samples, such as the inconsistent presence of matrix salts and organic compounds or different viscosities and surface tension of the liquid. Each of these can be overcome by the use of standard addition calibration techniques discussed in Chapter 6, but at a significant increase in the cost of analysis (primarily due to labor costs). For low ionic strength samples, nebulizer interferences are less prominent. Chemical interferences are common in FAAS and FAES but are less common or practically nonexistent in ICP-AES due to the relatively high temperature of the plasma, long residence time in the plasma, and inert atmosphere of the Ar plasma. Ionization interferences, in

direct arc and microwave produced plasmas, usually only occur for easily ionized elements such as alkali and alkaline earth elements. The net result of ionization interferences is an increase or decrease in the intensity of emission lines for these elements. Few ionization interferences occur for these elements in ICP. Spectral interferences can be common in high temperature plasmas as opposed to flame based systems given the complete excitation and subsequent emission of all compounds in the sample (including the argon). Spectral interferences can be divided into three different classes. The first type is spectral line coincidence when resolution of the monochromator of the system is too poor to separate the analyte line from a matrix line. The use of Echelle monochromators with higher resolution eliminates spectral interferences. The second cause of interferences occurs when a wavelength of interest overlaps completely with a nearby "broadened line wing". This can be solved by monitoring a secondary emission line for that particular element. Most instruments use a background correction technique to overcome this type of interference.

The final type of spectra interference referred to as spectral continuum occurs when stray light results from the recombination of electrons with Ar ions in the plasma that emits multiple intense lines. This can be avoided in some instruments by adjusting the temperature of the plasma or

monitoring alternate lines. Stray light from matrix emissions can be avoided by use of high end optical components such as “solar-blind PMT”.

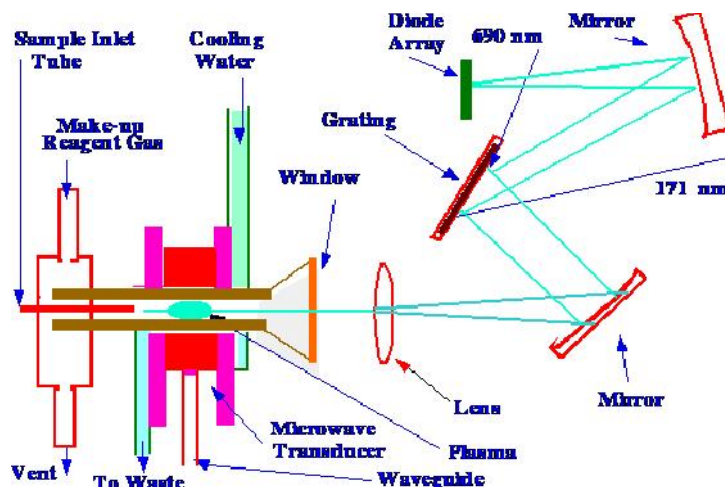


Figure 5: Schematic diagram of ICPS

4. Applications

- It has high temperature (700-900k) and high electron density (10^{14} - 10^{16} cm^{-3}).
- It is used for the high appreciable degree of ionization of elements.
- It is used applicable to the refractory elements.
- It is used for the excellent detection limit for most elements.
- It is a cost effective analysis.
- It is used high stability and accuracy purpose.
- It has low background emission and low chemical interference.
- It is used for the analysis of glass.
- It is used monitoring elements of interest in process solutions.
- It is used quantitative analysis of contamination of trace elements.

5. Summary and conclusion

Optical spectrometry has made considerable advances since the first flame based instruments were introduced in the 1960s. Recent advances in plasma technology, monochromator layout, and computer based detector systems such as charge transfer devices have given a new meaning to “state of the art” technology. Today low end FAAS instruments are only used in situations where only one or two elements are analyzed infrequently. High sample

through put situations, such as those found in industry and environmental monitoring; require automated systems that can perform multiple analyses in a minimum amount of time. But these demands are paid for with instruments of significantly higher cost. While ICPAES detection limits are significantly better than flame based techniques, mass spectrometry yields even better detection limits and can distinguish between different isotopes.

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