Dedicated axial or radial plasma view for superior speed and performance

Technical overview

Introduction

The superior design of the Agilent 700 Series ICP-OES instruments, which feature either an axially or radially-viewed plasma, results in better speed and performance than instruments with inferior dual-view optics and detection systems. With an optical system that provides full wavelength coverage in a single measurement, and a cooled-cone plasma interface that delivers exceptionally low matrix interference performance, the Agilent 700 Series is the world's only truly simultaneous ICP-OES. The superb performance of the Agilent 700 Series negates the need for dual-view optics, which were designed for the first generation of simultaneous ICP-OES systems utilizing solid-state detector systems to overcome design and technology limitations. Many of these limitations still exist today in some modern ICP-OES instruments.

Plasma configurations

To meet the application requirements of the analyst, most manufacturers of ICP-OES offer systems with various plasma configurations. The most common being:

- Vertically-oriented, radially-viewed plasma configuration.
- Horizontally-oriented, axially-viewed plasma configuration.
- Horizontally-oriented, dual-view (axial and radial) plasma configuration.

The choice of configuration, particularly between radially and axially-viewed plasma systems, is typically defined by the detection limit requirements of the analysis, and by the complexity of the sample matrix. Axially-viewed systems offer lower detection limits, whereas radially-viewed systems are preferred for routine analysis of more complex sample matrices. For oils, metals and geological samples, the detection limit of a radially-viewed system is usually sufficient, and the application easier and more routine to run.

Dual-view on the other hand is still a horizontally oriented plasma and although it offers a side-on (radial view), it does not offer the same benefits as a dedicated vertically oriented, radially viewed plasma.

The plasma

An inductively coupled plasma is created by the injection of a gas, usually argon, into a radio frequency generated magnetic field. A highly energized cloud of gaseous ions and electrons is formed. Sample is presented to the plasma, usually as an aerosol, where it is completely broken down by the high temperatures into its constituent atoms and ions.

The plasma has three distinct temperature zones (Figure 1), which can be clearly seen when a high concentration of yttrium is introduced. The three zones include the:

- Lower red 'bullet area', representing emission from atomic yttrium following desolvation, dissociation and atomization of the sample aerosol.
- Central blue 'analytical zone' representing emission from ionized yttrium atoms.
- Upper red and cooler 'plasma tail' representing emission from molecular species such as oxides of yttrium.

While the upper bullet area and analytical zone are analytically important, the cooler plasma tail is detrimental to analytical performance. Self-absorption of emitting atoms and ions reduces the linear range, while the cooler temperatures intensify matrix-related interferences such as ionization effects.

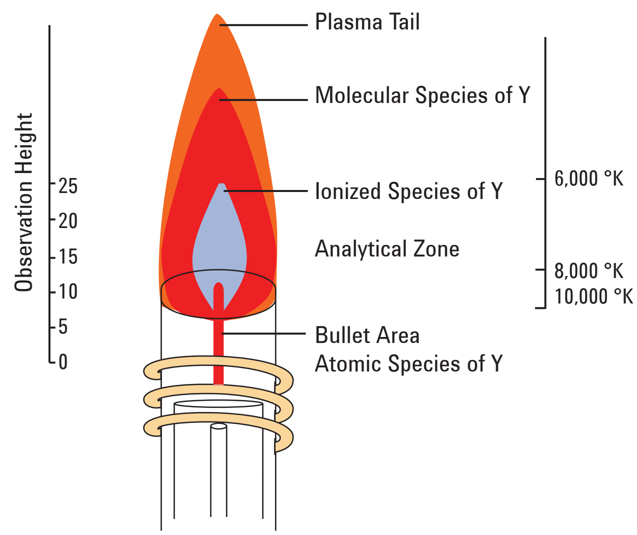


Figure 1. The various plasma regions and temperatures as viewed when aspirating a solution of 1000 mg/L yttrium into the plasma

Axially and radially-viewed systems

The first commercial ICP-OES instruments used a vertically-oriented, radially-viewed plasma system, whereby the plasma was viewed side-on by the optical system (Figure 2, top). Still commonly used today, such systems were found to be flexible and robust, providing excellent linearity and detection limits similar to or better than those achieved in flame atomic absorption spectroscopy (FAAS). The higher temperatures within the plasma also greatly reduced chemical and ionization interferences compared to FAAS.

As ICP-OES developed, the ability to optimize the viewing position and plasma conditions was seen as a major advantage. Analyte emission lines could be optimized for maximum sensitivity and minimum interference. With the cooler plasma tail outside the optical path, and the hot plasma gases flowing directly into the exhaust system, radially-viewed systems were, and still are, considered ideal for routine analysis of complex sample matrices.

The drive towards lower detection limits lead to the development of the horizontally-oriented, axially-viewed ICP-OES, where the plasma is viewed end-on (Figure 2, bottom). The increase in sensitivity compared to radial viewing provided a significant improvement in detection limits of 5 to 10-fold for most elements. The two biggest challenges faced by manufacturers in designing a horizonally-oriented, axially-viewed ICP-OES were:

- Protecting the pre-optics window from damage from the hot plasma gases.
- Increasing linearity and reducing matrix interferences by removing the plasma tail from the optical path.

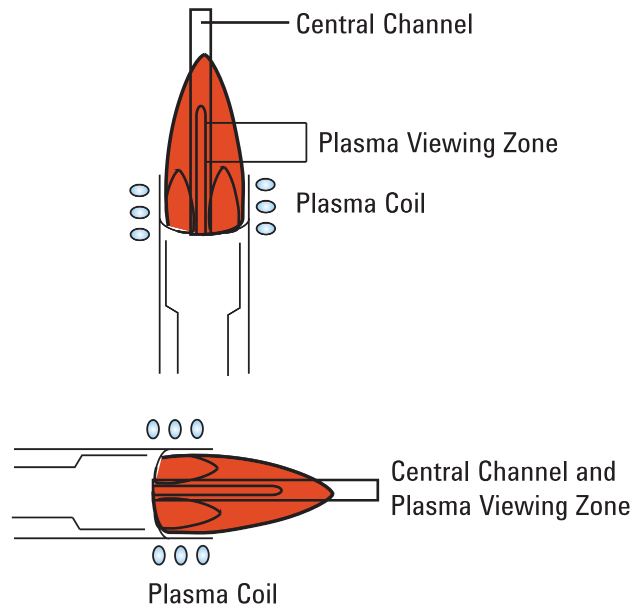


Figure 2. Vertically-oriented, radially-viewed plasma (top) and horizontally-oriented, axially-viewed plasma (bottom)

Axial plasma interface

These two challenges resulted in the emergence of three distinct plasma interface designs:

- A cone interface (Figure 3, top) where the plasma tail and heat is diverted away from the optical path. A small counter-flow or argon protects the optical window from heat, contamination and intrusion of air.
- A shear gas (or gas knife, Figure 3, middle) where a very high flow of gas such as air or nitrogen is used to displace the plasma tail from the optical path. Nitrogen is necessary for maximum transmission of low UV emission lines below 190 nm and flow rates of up to 20 L/min are required.
- An extraction system (Figure 3, bottom), which removes the heat of the plasma away from the optical window. A counter-flow of argon minimizes intrusion of air that reduces the sensitivity of elements with emission lines below 190 nm, including arsenic, sulfur, phosphorus and aluminium.

The shear gas and cone interface designs provide both protection of the optical window and removal of the plasma tail from the optical path. With an extraction system, the optical window is protected but the plasma tail is not eliminated from the optical path. Therefore, a reduction in the linear dynamic range and an increase in ionization (matrix) interference results with such a design.

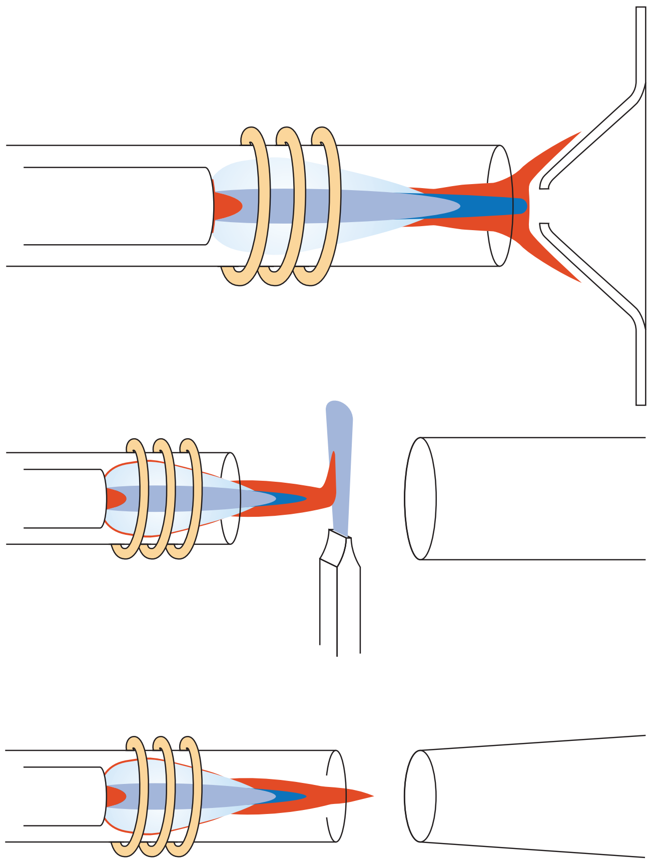


Figure 3. Examples of plasma interfaces used in modern ICP-OES instruments. Top: A cooled cone interface deflects the plasma tail (red) away. Middle: A shear gas blows away the plasma tail. Bottom: A vacuum exhaust removes the plasma heat only.

Matrix interferences

The most common form of matrix interference observed within the plasma is 'ionization interference', also known as 'easily ionized element' (EIE) interference.

Ionization interferences result from the presence of high concentrations of easily ionized elements in samples, especially the common alkali elements, potassium and sodium, and to a lesser extent, the alkaline earth elements, calcium and magnesium. These elements have low energies of ionization and are easily ionized by the high plasma temperatures. At sufficiently high concentrations, the electron density within the plasma is increased to a level where the atomization-ionization equilibrium of other elements is affected. This is one of a number of important reasons why matrix matching of calibration and sample solutions is often recommended, although it is not always possible.

The effect EIEs have when present in samples at increasingly higher concentrations is either enhancement or suppression of the emission signal intensity, resulting in the reporting of either false-high or false-low element concentrations. Most elements typically experience signal suppression, while the atomic emission lines of alkali and alkaline earth elements tend to exhibit signal enhancement. Elements exhibiting suppression can often be corrected for by the inclusion of a suitable internal standard element. The elements yttrium, scandium, and indium are commonly used for internal standard correction.

The varying degree of signal enhancement observed by alkali and alkaline earth elements makes it difficult to find a suitable internal standard for these elements. The use of an ionization buffering element such as cesium, common in FAAS, can significantly reduce ionization interference effects. Cesium itself is an EIE and its addition to all analysis solutions negates (buffers) the effects of other EIEs that may be present in samples. Cesium is an ideal buffering element as not only is it easily ionized, its emission intensity is also very weak in ICP-OES and is therefore unlikely to cause spectral interference on other elements. Cesium is available in a highly pure form and is significantly cheaper to use compared to the cost of additional argon usage when operating in dual-view mode. Lithium is a popular alternative, particularly when cesium is an analyte of interest.

The addition of an ionization buffer and internal standard to analysis solutions is greatly simplified by preparing a single buffer/internal standard solution and adding it online to the sample stream.

It should be noted that all elements are influenced by ionization interferences to some extent when the concentration of EIEs in a sample is sufficiently high. This phenomenon occurs in both radial and axial viewing modes, although the interference is more prominent on axially-viewed systems.

The Agilent cooled-cone plasma interface

As previously stated, three distinct approaches have been taken to displace the cooler plasma tail from the viewing optics.

The innovative cooled-cone interface (CCI) of the Agilent axially-viewed ICP-OES exhibits much lower EIE effects compared to competitive systems using either a shear gas or vacuum exhaust. In addition to deflecting the plasma tail away from the optical path, the CCI also eliminates the sudden temperature gradient present on the shear gas interface, further reducing ionization interferences and maximizing the linear dynamic range.

Regardless of the interface, eventually there will come a point when ionization interferences become appreciable and a means of eliminating them will be necessary, whether by matrix-matching calibration standards and samples or using an ionization buffer solution.

Dual-view systems

By the 1990s, dedicated radially-viewed ICP-OES with photomultiplier tube detection systems were well established. The introduction of solid-state detectors (CCD, CID) was followed closely by the first axially-viewed systems. Serious limitations with these first generation detectors, including the limited wavelength coverage of segmented detectors, encouraged the development of dual-view optics. Without access to less sensitive wavelengths, the linear dynamic range was compromised. Dual-viewing was able to alleviate this to some extent by providing an additional order of magnitude linear dynamic range via a separate, side-on measurement.

Originally targeted at environmental samples, side-on (radial) viewing also lessened the effect of ionization interferences that were more pronounced on these earlier axial plasma interface designs.

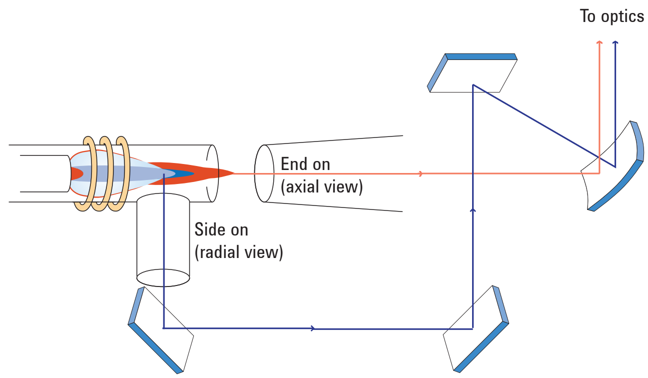


Figure 4. Diagram of the optics that allow side-on viewing of the plasma, inferior to a dedicated radial system.

The concept of dual-view itself has a number of shortcomings, especially when compared to superior designed, dedicated axial and radial systems. For example:

- Dual-view measurements must be taken separately thereby increasing analysis time and running costs. Furthermore, some ICPs require additional measurements to cover the entire wavelength range. Therefore a simultaneous instrument becomes a sequential one.
- Separate analyte calibrations and internal standard correction measurements are required for each view. Solutions preparation time is increased and some standards may need to be analyzed twice in both viewing modes.
- The ability to adjust the side-on (radial) viewing position is restricted or unavailable making it difficult to optimize for reduced interferences and maximum sensitivity.
- The plasma conditions, gas flows and torch geometry for optimum axial performance are significantly different from a radially viewed plasma. A dual view arrangement results in a significant compromise to one or both of the views.

Dedicated axial and radial systems from Agilent

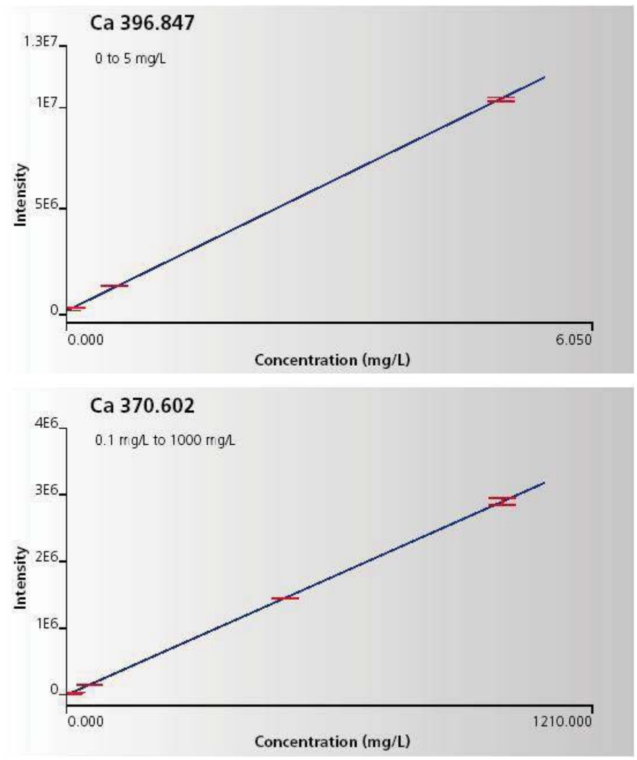
So why does Agilent offer dedicated axially and radially-viewed systems, but not a dual-view system? The answer is: superior design and technology. This superiority in the areas of plasma generation, plasma interface, and in the optical and detection systems, removes many of the limitations that dual-view was designed to overcome. The inclusion of dual-view optics on the Agilent ICP-OES would actually compromise performance.

The Agilent 700 Series ICP-OES has been designed with ultimate speed and performance in mind. The computer-optimized echelle optical system uses fewer components for high light throughput, low detection limits and excellent spectral resolution. The echelle image produced by the optical system is focused onto a single CCD detector allowing the entire wavelength range from 167 to 785 nm to be captured in a single, truly simultaneous measurement. The unique CCD detector uses superior technology enabling all elements to be measured at the same time. With access to more than 33,000 listed wavelengths, strong, moderate and weak emission lines can be used to measure from parts-per-billion to percentage levels in one truly simultaneous measurement.

With superior technology comes superior software features. For example, MultiCal offers extended linear dynamic range and results verification. Figure 5 (a and b) shows a calcium calibration from 0 to 1000 mg/L using a combination of the very sensitive 396.847 nm and less sensitive 370.602 nm wavelengths. The results are shown in Figure 5 (c). The first column in the table reports the average in-range result of the three Ca wavelengths in the determination of trace, minor and major levels of Ca in waters and effluents.

a

b



c

Sample Labels	Ca Mean mg/L	Ca 396.847 mg/L	Ca 315.887 mg/L	Ca 370.602 mg/L
Clean water blank	0.00082	0.00082		
River water	0.811	0.805	0.810	0.817
Sewage effluent	29.64		29.47	29.80
Industrial effluent	30.25		30.20	30.29
Bore hole water	175.0		175.1	174.9

Figure 5. The innovative Agilent ICP Expert II software feature 'MultiCal' extends linear dynamic range and confirms results. a) A Ca calibration from 0 to 1000 mg/L using a combination of the sensitive 396.847 nm and b) less sensitive 370.602 nm wavelengths. c) Combine the Ca 396 nm, Ca 315 nm and Ca 370 nm emission lines to extend the linear dynamic range and confirm results are free from interference.

Summary

Compared to dual plasma view ICP-OES instruments, dedicated axially or radially-viewed Agilent 700 Series ICP-OES instruments perform better and faster.

In the axially-viewed 700 Series ICP-OES, an innovative cooled-cone interface removes the plasma tail, thereby increasing linear dynamic range and decreasing matrix interferences such as easily ionized element effects. The cooled-cone interface also protects the pre-optics window from the hot plasma gases. When optimum sensitivity is required, the axially-viewed 700 Series is the instrument of choice.

In the radially-viewed 700 Series ICP-OES, the plasma tail is outside the optical path and the hot plasma gases flow directly into the exhuast. The radially-viewed 700 Series ICP-OES is ideal for routine analysis of complex sample matrices.

Whichever view you choose, unlike dual-view ICP-OES, the 700 Series decreases analysis time and running costs. Superior optics enable full wavelength coverage to be performed in a single measurement, making the 700 Series the world’s only truly simultaneous ICP-OES. Exceptional plasma generation, plasma interface, optics and detection removes many of the limitations that dual-view was designed to overcome.

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