



The Latest Advances in Axially Viewed Simultaneous ICP-OES for Elemental Analysis

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Background

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a popular technique of elemental analysis. ICP is applicable to around 73 elements and provides fast multi-element analysis with superior detection limits to atomic absorption spectrometry (AAS) for many elements.



Agilent Technologies

Initially ICP-OES systems featured a vertically-oriented plasma. The plasma was "viewed" by the optical system from the side, Figure 1. This configuration is known as "radial viewing" and has the advantage of providing immediate venting of exhaust gases and waste heat to an overhead extraction system. In the mid 1970's workers began to develop end-on or axially viewed plasma systems [1]. The aim of axial viewing is to observe a longer path length in the analyte-rich central channel, while avoiding viewing the surrounding intense argon plasma [2]. This approach provides improved signal to noise ratio and hence better detection limits. Axially and radially viewed plasmas are shown schematically in Figure 1.

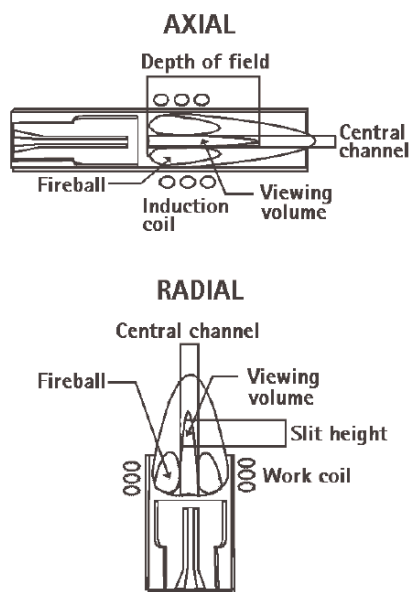


Figure 1. Schematic diagram of radial and axially viewed plasma systems, note the three concentric tubes of the torches, the vertical orientation and side viewing of the "radial" torch and the horizontal orientation and end-on viewing of the "axial" torch.

Axially viewed plasma systems find application where best sensitivity is needed, particularly environmental analyses of waters and wastes. Axially viewed ICP-OES offers a viable and more robust alternative to more expensive ICP-Mass Spectrometry systems while meeting the detection limit requirements of most regulatory bodies. Historically, the performance of axially viewed ICP systems was thought to be limited by injector tube blockage and subsequent signal drift when solutions containing high dissolved solids are aspirated. In addition, the limitations of older ICP detector designs meant that the linear dynamic range of axial ICP was

restricted to upper concentration limits of just 10–100 parts-per-million. This linear dynamic range problem spurred interest in "dual viewed" plasmas - a horizontal plasma viewed alternately from the end or from the side. Dual viewed systems however require samples to be analyzed twice - once with each viewing mode, and so productivity is restricted.

The reputation of axial ICP systems has unfortunately been undermined by these historical observations. The purpose of this paper, is to review the latest advances in ICP-OES detectors, software and sample introduction systems which lead to modern simultaneous axially viewed ICPOES systems that overcome these perceptions. Today's modern axially viewed ICP systems provide the productivity of a single analysis with wide dynamic range from one plasma view.

Advances in ICP-OES Detector Design

Early ICP designs used photomultiplier tubes (PMT) to detect light emitted from the plasma. PMTs could be used in either simultaneous ICP systems, with multiple detectors being placed around a Rowland circle or coupled to a sequential scanning monochromator such as a Czerny-Turner design. The disadvantages of each of these approaches is clear - using discrete detectors to measure each wavelength means you have to choose the wavelengths to measure ahead of time - restricting future flexibility. Sequential scanning designs, while more flexible, require more time to complete an analysis.

In the early 1990s various groups developed solid state simultaneous detection systems either based on Charge Coupled Devices (CCD) or Charge Injection Device (CID) designs. These devices differ in the way in which they measure the electronic charge created on the surface of the detector. A useful review of these technologies was provided by Harnly and Fields in 1997 [3]. With both detector types, an array of light sensitive detectors or pixels is used to convert the incoming photons into electrons for measurement.

These detectors are generally used in conjunction with an echelle polychromator which creates a 2 dimensional spectrum from the light emitted by the plasma. The emitted light is split both into its component optical orders (creating a series of "rows" of light) and also into its component wavelengths. One CCD design implemented in the early 1990s positioned the light sensitive pixels at the locations of preferred wavelengths [4]. This design became known as the Segmented

Array CCD detector or SCD. Pixels were created in small linear groups positioned to detect the preferred suite of wavelengths. The SCD used just 6336 pixels, presumably in an attempt to minimize perceived limitations in "readout speed and photometric data quality". The restricted number of pixels no doubt matched the limited data processing capabilities of the electronics and computers then in use. The SCD is still used today with a current ICP-OES design. The limitations of the SCD are clear - pixel groups are positioned only at locations of preferred wavelengths - thereby imposing the same restrictions of wavelength choice and flexibility as the multiple PMT based designs of the 1970s and 1980s. Barnard et. al. [4] state that the SCD provides only "5.7% coverage of the spectrum from 167 to 782 nm". Because of this inherent restriction on available wavelengths current ICP designs based on SCD technology cannot take advantage of the improvements in linear dynamic range that can be obtained by using multiwavelength data. As a result, alternative plasma viewing methods, such as the dual view systems, were developed to compensate for this lack of linear dynamic range.

The Vista series of simultaneous ICP-OES spectrometers were introduced in 1998. In developing the Vista series, Agilent took advantage of the availability of the next generation of CCD detectors [5]. The VistaChip (Figure 2) CCD features over 70,000 pixels positioned to exactly match the free spectral range of the two dimensional echellogram. Zander et. al. [5] referred to this as "image mapping", with the pixels being positioned so as to match the exact angle

and alignment of 70 orders of light coming from the echelle spectrometer. The placement of the pixels in continuous rows provides complete and continuous wavelength coverage of 96% of the analytical spectrum. This approach opens up a major advantage of ICP-OES - using alternative wavelengths to avoid spectral interferences and to extend linear dynamic range by using wavelengths in combination.

In August 2000, the world's first array CCD detector applied to simultaneous ICP-OES with the Vista- MPX was announced. The MPX detector features over 1.1 million pixels arranged in an X-Y array - again providing up to 96% coverage of the analytical spectrum from a single simultaneous reading. The Vista-MPX achieves the linear dynamic range and flexibility advantages of the Vista image mapped CCD, in an even more affordable package. Both systems provide the advantages of true simultaneous ICP-OES, with simultaneous background correction and internal standardization providing more accurate and precise results. In addition, the systems include no moving optical components, resulting in excellent long term stability and analysis speeds compared to sequential scanning systems. The grating and prism of the echelle spectrometer used in the Vista series are fixed and the optics thermostatted providing long term drift-free performance without the need for correction lamps. With most axial and dual view systems the ICP torch is oriented horizontally and viewed end-on (Figure 1). This orientation is preferred because end-on viewing of a vertical (radially viewed) plasma is more difficult due to hot, corrosive vapors travelling past the viewing optics.

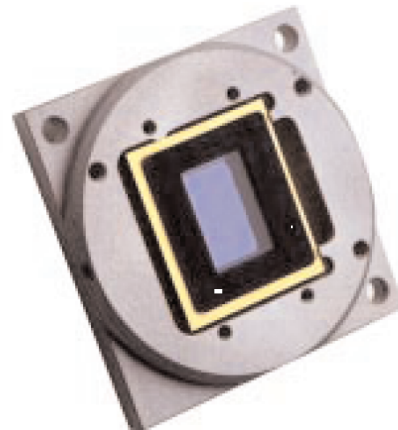
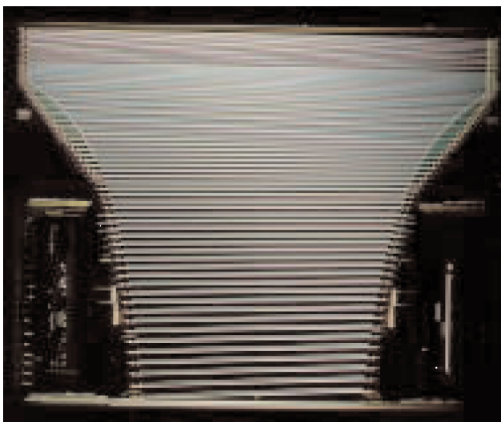


Figure 2. The Agilent VistaChips - the Vista Pro CCD (left) and the Vista-MPX CCD (right). The Vista Pro CCD image shows the continuous lines of pixels (photosensitive detectors) exactly positioned to match the spectral output from the echelle spectrometer. Note the differing slopes and separations of these "diagonal linear arrays" of pixels. The Vista-MPX CCD (right) is an array detector with over 1.1 million pixels in an X-Y grid.

Advances in Axial Viewing Systems

The Horizontal, Axially Viewed Plasma

- Offers 4–10x improvement in sensitivity compared to the radial view, due to longer path length of measurement
- Is ideal for routine analysis of samples containing less than 5% dissolved solids. With simple modifications to the sample introduction system Agilent axial ICP now can analyze 25% dissolved solids solutions directly for 24 hours.
- There are key differences between axially viewed plasmas. Agilent's Cooled Cone Interface (CCI) displaces the cooler tail flame of the plasma away from the optical path, resulting in greater linear dynamic range and a significant reduction in atomization and recombination interferences.
- Agilent's CCI requires only a small counter flow of argon gas, 2.5 L/min. The alternative shear gas approach used on many dual view systems requires very high volumes of gas, from 15-20 L/min, to displace the plasma from the optical path. This gas must be nitrogen to measure below 190 nm.
- Agilent's CCI design makes the axially viewed plasma ideal for analyzing organic solvents.

The axially viewed plasma provides the benefits of improved sensitivity and detection limits and this performance has seen this configuration grow in popularity in the past decade. Table 1 shows the improvement factors in detection limits that can be obtained using axial viewing compared to radial viewing, typically this factor is between 4–10 times. Axially viewed ICP systems achieve detection limits that meet the majority of requirements for drinking water, waste water and other important environmental applications. The axially viewed ICP easily meets the detection limit requirements of the US EPA [6] for example.

Table1. Comparison of 3 σ Detection Limits for Radially and Axially Viewed Vista-Pro ICP. All Data was Collected Using 30 Seconds Integration Times [7]

Element	Wavelength (nm)	3 σ Detection Vista-PRO radial ($\mu\text{g/L}$)	Limits Vista-PRO axial ($\mu\text{g/L}$)	Improvement factor
Ag	328.068	1	0.3	3.3
Al	167.016	0.9	0.2	4.5
As	188.979	5	1.5	3.3
Au	267.595	5	1.0	5
B	249.773	0.6	0.1	6
Ba	455.403	0.15	0.03	5
Be	234.861	0.05	0.01	5
Bi	223.061	6	2	3
Ca	396.847	0.06	0.01	6
Cd	214.438	0.6	0.05	12
Ce	418.660	2	2	1
Co	238.892	1	0.2	5
Cr	267.716	0.9	0.15	6
Cu	327.396	1	0.3	3.3
Fe	259.940	0.8	0.1	8
K	766.490	4	0.3	13.3
Li	670.784	1	0.06	16.7
Mg	279.553	0.04	0.01	4
Mn	257.610	0.08	0.03	2.7
Mo	202.030	2	0.5	4
Na	589.592	2	0.15	13.3
Ni	231.604	1.4	0.3	4.7
P	177.432	5	2	2.5
Pb	220.353	5	0.8	6.3
S	181.971	10	5	2
Sb	231.147	5	2	2.5
Se	196.026	6	2	3
Si	251.611	2.2	1.4	1.6
Sr	407.771	0.05	0.01	5
Ti	334.941	0.2	0.1	2
Tl	190.790	6	2	3
V	292.402	0.7	0.2	3.5
W	207.911	3.5	2	1.8
Zn	213.856	0.8	0.2	4
Zr	343.823	0.9	0.3	3

The Agilent axially viewed ICP systems all share the same viewing configuration, shown in Figure 3. The plasma is directed at a Cooled Cone Interface (CCI), consisting of a water cooled nickel cone with a large sampling orifice cut in its tip. A small counter flow of argon gas passing through the cone ensures that the heat and vapors from the plasma cannot compromise the optical system, which is further protected by a quartz window. The CCI displaces the cooler plasma tail away from the optical path of the ICP instrument. It is in this cooler region of the plasma that analyte self-absorption, vaporization and ionization interferences can occur. Brenner and Zander concluded [8] that "removal of the cool fringe reduces matrix effects due to Easily Ionizable Elements and Ca and extends the linear range of calibration and determination."

High Solids Capabilities

The axially viewed ICP provides excellent long term stability for samples containing up to 5% dissolved solids using standard sample introduction systems. With normal rinsing routines, these samples can be analyzed throughout the day using an axially viewed ICP. Most samples fall below this high dissolved solids limit. For example, if 1g of sample is digested and diluted to 100 mL this represents 1% dissolved solids in the sample. Figure 4 shows the long term stability of the Agilent axially viewed Vista ICP for the continuous analysis of 5% sodium chloride solution [9].

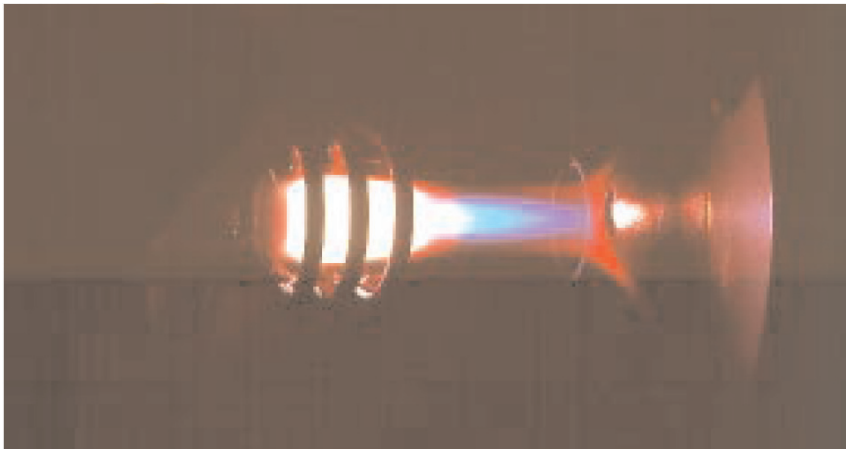


Figure 3. Photo of Agilent's Cooled Cone Interface. The cooler red zone of the plasma can be seen displaced around the outside of the cone, while aspirating Yttrium. The large central hole in the cone allows the optical system to observe the central channel of the plasma. A counter flow of argon gas and a sealed optical window behind the cone, protect the optical system.

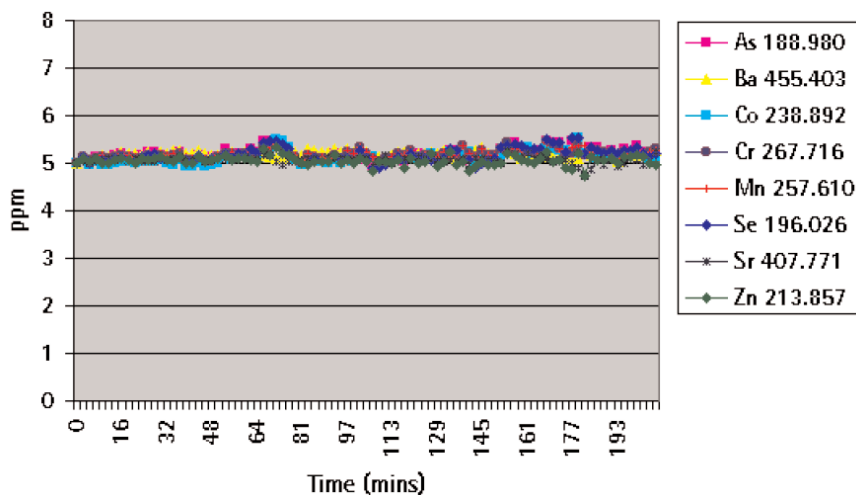


Figure 4. The stability of a range of elements from a continuously aspirated solution of 5% NaCl using the Agilent Vista-MPX simultaneous ICP-OES. Percent standard deviation over a period of 3.5 hours was less than 2.5% in all cases. Note this analysis was conducted without between-sample rinsing which would further extend operation time.

Recently, a range of new spraychamber, nebulizer and torch options has been developed for ICP-OES which allows longer analysis periods for higher levels of dissolved solids. These options include double pass spraychambers, "v-groove" nebulizers, wider bore injector tubes and demountable axial torch designs. By simply selecting appropriate sample introduction system components, long term analysis of high levels of dissolved salts is now obtainable. An example of this work is shown in Figure 5 [10]. Using a modified torch with an axially viewed Vista-MPX simultaneous ICP-OES, the direct analysis of 25% sodium chloride solutions was demonstrated for over 24 hours of continuous aspiration. The precision over 24 hours ranged from 3.3% to 5.2% relative standard deviation. This work shows that the high salts stability of the Agilent axially viewed ICP's is dependent upon the choice of sample introduction system and not on the instrument itself. In this way, the performance of a radially viewed ICP can be obtained from an axially viewed ICP without the need for dual view optics.

Linear Dynamic Range

Linear Dynamic Range (LDR) is an important performance characteristic of ICP spectrometers as it defines the upper and lower limits of analyte concentrations that can be accurately measured. The lower end of this scale is defined by detection limits (see Table 1) or determination limits and the upper end is defined by the limits of calibration linearity. The US EPA [6] uses a 5% calibration accuracy definition to determine this upper concentration limit. LDR limitations are often cited as the need for dual view plasma systems - that is, it is claimed that to measure high levels of analytes (> 100 mg/L) both the radial view and the axial view are required in the one spectrometer. Since both views cannot be measured simultaneously, the dual view approach slows down the productivity of the analysis.

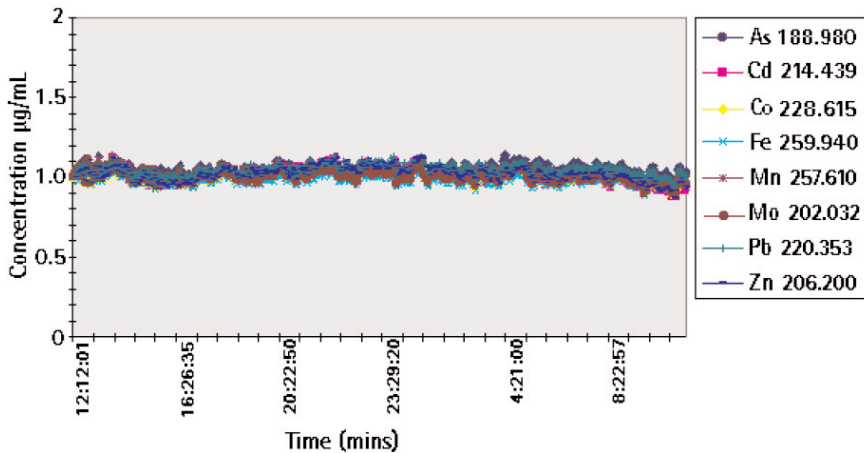


Figure 5. The continuous analysis of 25% sodium chloride solution over 24 hours using a Vista-MPX axially viewed ICP (expected concentrations 1mg/L). The solution was continuously aspirated without rinsing and no internal standard correction was used. The plasma torch was fitted with a high solids injector tube. A Sturman Masters double pass cyclonic spraychamber and v-groove nebulizer were used with an argon saturator accessory (ASA).

As noted earlier, many of the assumptions about the linear dynamic range of ICPOES systems may have been based upon detector and plasma interface design limitations of that era [4]. With the introduction of Agilent's Cooled Cone Interface (CCI) these limitations have been overcome and it is possible to have wide linear dynamic range from one axially viewed plasma system without the need to analyze the sample twice. In the past, the linear dynamic range of axially viewed systems was limited by analyte self-absorption due to the longer path length of measurement. The Agilent CCI provides extended linear dynamic range by optimizing the observation of the central channel of the plasma and eliminating observation of the cooler plasma tail.

When coupled with the full wavelength coverage of the Agilent ICP-OES systems, the axially viewed configuration can be used from parts-per-billion detection limits up to maximum concentrations of percentage levels. This performance is shown in Table 2 [12], which shows the upper limits of linear dynamic range for elements using the axially viewed, simultaneous Vista-MPX. Comparing these results to the detection limits in Table 1, it can be seen that a very wide dynamic range can be obtained from one axially viewed ICP system with just one sample measurement.

Table 2. *Linear Dynamic Range Test Results on the Axially Viewed Vista-MPX with CCI, Showing Accurate Recoveries of Elements up to 500 and 600 mg/L is Easily Possible. Vista CCI Provides Radial View Performance with the Benefits of Axial Sensitivity*

Element	LRA (mg/L)	Recovery %
Ag 328.068	10	101
Al 236.705	500	99
Al 308.215	40	100
As 188.980	10	103
Ba 585.367	200	95
Be 313.042	5	101
Ca 315.887	100	99
Ca 370.602	600	97
Cd 226.502	5	99
Co 228.615	50	97
Cr 267.716	20	100
Cu 327.395	30	101
Fe 234.350	100	100
Fe 258.588	500	95
K 404.721	500	104
K 766.491	50	102
K 769.897	200	101
Mg 279.800	600	98
Mg 383.829	600	99
Mn 257.610	50	97
Na 330.237	600	97
Na 589.592	50	98
Ni 231.604	50	97
Pb 220.353	100	101
Sb 206.834	10	103
Se 196.026	100	101
Tl 190.794	100	101
V 311.837	60	99

Advances In Software Design

To take advantage of the full wavelength coverage of Agilent's CCD detector technology, the Vista simultaneous ICP systems feature MultiCal, which automatically assigns each sample to the best wavelength for that result. If a sample result falls within a particular concentration range it is automatically assigned to the wavelength that is most appropriate for that concentration. In this way the Vista series of instruments takes advantage of the availability of all of the wavelengths in the analytical spectrum - automatically combining the most sensitive wavelengths for best detection limits with less sensitive wavelengths for best dynamic range.

Figure 6, shows the MultiCal advantage, with a pair of calibration graphs for calcium, measured on the Vista-MPX. Low concentration results are automatically reported from one calibration graph and high concentration results reported from a second calibration graph - extending the linear dynamic range for this element. Also in this example, the results from the two wavelengths have been mathematically combined into one calcium result. In this case the average of the two calcium results from the two wavelengths has been used, however users may also choose from weighted mean, minimum and median of the results. Only results that fall within the valid calibration range of the wavelengths will be used in these calculations – providing extra surety of data quality. The original wavelength columns can either be displayed (for full information) or hidden (for simplicity and ease of use). By displaying all available wavelength information, the user is given another data quality control check, by comparing the accuracy of the results from two or more wavelengths for the same element.

Conclusions

In this paper we have reviewed the recent developments in the design of axially viewed ICP-OES. Axially viewed ICP-OES has emerged as the preferred viewing technique due to its benefits of enhanced sensitivity and detection. Agilent's Cooled Cone Interface is an optimized design that eliminates chemical and molecular interferences and extends the linear dynamic range of the axial ICP. This axial design combined with Agilent's CCD detector technology provides simultaneous measurement of all wavelengths and further extends the linear dynamic range of ICP-OES. With simple changes to the sample introduction system, Agilent's axially viewed ICP-OES can analyze high dissolved salt samples continuously with excellent long term stability.

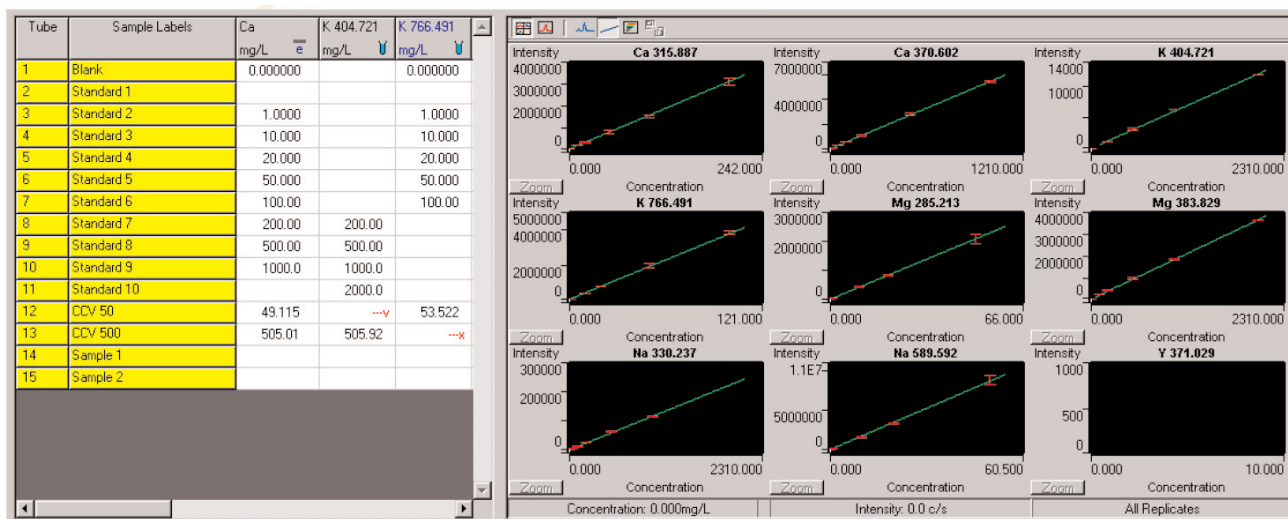


Figure 6. The Agilent MultiCal advantage - the first column shows the mean result from two Ca wavelengths - 315.887 and 370.602 nm, automatically combined by the Vista-PRO software. The combined wavelengths allow calibration to 1000 mg/L from a single analysis on this axially viewed ICP. This extended linear dynamic range would normally only be possible with a radially viewed ICP. With MultiCal, the Vista ICP series provides both the extended linear dynamic range of a radial ICP and the excellent detection limits of an axially viewed ICP with one simple analysis. The accuracy of the results is established from the 50 mg/L and 500 mg/L Continuing Calibration Verification (CCV) results.

The unique MultiCal automates the intelligent assignment of sample results to the most appropriate wavelength. The accurate measurement of high concentration matrix elements can now be performed simultaneously with trace level detection of other analytes of interest from one axial plasma viewing system and one measurement. MultiCal eliminates the need for Dual View optics, enhances productivity and reduces argon consumption.

Agilent's CCI and MultiCal approach offers significant advantages that should see axially viewed ICP-OES remain a popular technique for many years to come.

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