

# Re: Viewing Atomic Spectroscopy

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## Samples containing high dissolved solids require looking at ICP from another angle.

Inductively coupled plasma (ICP) spectrometers have been successfully used for years to determine major and minor constituents in a variety of samples (see box, "Plasma Science"). The sample may be any liquid or suspension of solid particles that can be atomized through a nebulizer. The markets served include aerospace, automotive, chemical, environmental, food, geological, metallurgical, paints and coatings, petrochemical, pharmaceutical, precious metals, and semiconductors.

The ICP instrument includes a power source (radio frequency generator), sample introduction system, spectrometer, detector, electronics, and software. Each portion of the instrument can be designed in various ways, each of which has distinct advantages and disadvantages. A common sample introduction system features a nebulizer and spray chamber that provide a sample aerosol traveling to the plasma via a torch. The relative advantages and disadvantages of the position of this torch—horizontal or vertical—and the viewing of the plasma—axial or radial—have prompted much discussion (Figure 1).

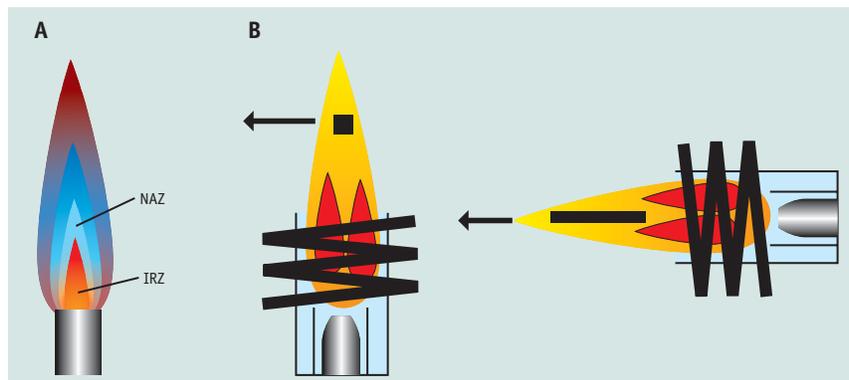
When the sample is something other than a relatively clean water sample, dissolved solids, organic constituents, and other contaminants can complicate sample description. These problems are sometimes intensified when the ICP instrument uses an axial plasma with a low- to mid-resolution spectrometer.

Depending on the sample type, however, the advantages of high-end ICP units can be fully utilized. As the level of dissolved solids in a solution increases, so does the possibility of difficulties with instrument detection limits, accuracy, and stability. This problem is magnified in ICP spectrometers that use an axial plasma design.

### Improving Performance

Researchers discovered that axial plasma suffered from serious interferences caused

mainly by ionization difficulties, which led to erroneous results that required further laboratory work for validation and quality control (1, 2). To address this issue, researchers worked on the special requirements of axial ICP needed to improve the instrument's performance. A primary need was to eliminate the fireball region of the plasma while allowing researchers to view



**FIGURE 1:** (A) The plasma flame is composed of several regions, including the initial radiation zone (IRZ) and the normal analytical zone (NAZ). (B) Depending on the ICP unit, the plasma can be studied from either a radial view (left) or an axial view.

just the central channel. This was largely accomplished with improved optical baffling. The new optical baffling and better resolution improved performance with respect to noise for the radial ICP instruments as well, but for most spectrometers, these changes severely restricted the signal, so gains in detection limit were small. Insufficient signal due to the optics has not prompted improvements in radial ICP instruments, except for the highest-resolution ICP spectrometers with large optical components.

Recent work on high-resolution, high-optical-efficiency ICP spectrometers has improved the detection limits of radial ICP units more than 10-fold compared with low-resolution ICP instruments and has yielded better than published detection limits on axial ICP units (3). Today, high-resolution spectrometers provide detection limits at or below the single part-per-billion

range using a radial plasma configuration, while low- to mid-resolution systems are in the 1.5- to 5-ppb range for axial plasma configurations and 5 to 50 ppb for a radial configuration.

Light throughput is a key parameter in the amount of signal and, hence, the detection limit. Stray light raises the background and thus increases noise and background equivalent concentration, which has a direct effect on the detection limit. This is one of the limiting factors for spectrometers using solid-state detectors because of the

required echelle optical system, which typically produces high stray light, in part from the use of very high optical orders of light (4).

### Radial vs Axial Viewing

Depending on the resolution of the spectrometer, axial ICP instruments can have improvement factors varying from 10 times down to 2–3 times compared with radial ICP. The improvements in detection limit may be useful for simple, clean environmental samples, albeit with a modest increase in cost. However, radial ICP instruments have been shown to be more robust than axial ICP spectrometers. The Mg ion/atomic line test promoted by Jean-Michel Mermet is a good measure of the "robustness" of the plasma system to different solutions that may present various interferences in the plasma (5). This ratio

**TABLE 1: Stability the Following Day and After Five Days**

Calcium	Simultaneous internal standard				Sequential internal standard			
	Following day		After five days		Following day		After five days	
	Conc. (%)	RSD (%)	Conc. (%)	RSD (%)	Conc. (%)	RSD (%)	Conc. (%)	RSD (%)
Before recalibration	44.09	0.14	46.13	0.11	45.85	0.28	45.86	0.048
After recalibration	45.56	0.064	45.37	0.065	45.39	0.15	45.45	0.06

provides the ability to assess a robust plasma, which will give fewer interferences. This is especially important when the solutions contain complex matrices and high amounts of dissolved solids. The size of the normal analytical zone (NAZ) analyzed by the instrument can affect the accuracy and recoveries obtained in any tests. Some spectrometers view a small region of the plasma, so the viewing height becomes an important parameter to optimize. The NAZ (Figure 1) is above the bullet region or initial radiation zone (IRZ). It is easy to avoid this region in radial ICP, but in axial ICP spectrometers, the IRZ and a longer path length of the NAZ are both viewed.

For axial ICP instruments, the outer tube

of the torch has to be longer to contain the plasma, which presents problems (as in ICP-MS) with dissolved solids. The salts attack the outer tube and can increase consumable costs dramatically in some cases. For some samples (e.g., brines, fusions, and other high-dissolved-solid solutions), the axial torch may only last days. For axial ICP, there is another parameter to be considered. The plasma region above the NAZ contains element oxides as the plasma loses temperature and combines with the air. Manufacturers often use a shear gas, usually compressed air, to create a curtain that cuts off viewing this region. The shear gas for elements below 190 nm requires nitrogen, which represents an added cost. An

alternative method is to have a cone within the plasma, similar to ICP-MS. The plasma is viewed without any oxide contribution and thus has better background and less interference. This method also offers the advantage of being able to determine elements in the low-UV range. However, argon consumption increases, on average, an extra 2.5 L/min.

Typically, with high-dissolved-solids samples such as cement, NaOH, and NaCl, researchers using instruments with an axial plasma must dilute the sample to 1–3%, and even then they may experience

### Plasma Science

ICP is an atomic emission technique, which measures the energy lost by an atom passing from an excited state to a lower energy state. The atomic emission spectrum is composed of discrete spectral lines:

- Line I is caused by emission from an un-ionized atom,
- line II is caused by emission from a singly ionized atom, and
- line III is caused by emission from a doubly ionized atom.

Lines I and II are frequently observed, whereas line III is rarely observed, and lines of a higher degree are not observed because of the energies involved. The number of photons emitted is proportional to the number of atoms of the element present. To be excited, the sample must be atomized, meaning dissociated into free ions or atoms.

The emission phenomenon takes place in a plasma, which is an electrically neutral, highly ionized gas—typically argon—that is formed when argon flows through a crystal tube inside a solenoid. Lines of force, generated by magnetic fields, are directed along the axis of the solenoid inside the tube and take the form of an ellipse on the outside. An electrical discharge is created to arc the plasma by partially ionizing the gas in the torch. The electrons produced are subjected to the magnetic field and circulate along the axis of the crystal tube describing annular circuits, producing induced or eddy currents. Collision of gas atoms with the electron path results in their heating and ionization, and thus, the plasma is self-maintaining and continuous.

problems with elements such as Ba, Ca, Mg, K, Cd, Cr, and Mo unless matrix matching is used.

Radial-view ICP offers fewer matrix effects than axial viewing, because the IRZ is not viewed and can be avoided by changing the viewing height. Radial viewing results in fewer spectral interferences, especially with organics, because observed band structures are reduced. No torch adjustment is required for each element if you view the entire NAZ, and because the RF power and plasma gas are generally lower, any sample matrix can be run on radial-view ICP.

More recently, dual-view systems have been marketed using three mirrors. It should be noted, however, that each mirror loses 5–10% signal as a compound loss. The dual-view system is optimized for axial view, so the torch is positioned in a horizontal plane. The torches used for dual view are longer, which means problems such as reduced dissolved solids capability, salt causing faster blockage, and contamination around the torch can have a cumulative effect in reducing the long-term stability.

### Proof of Principle

Chemical analysis of cement is an interesting application for ICP spectrometry (6). The cement industry requires analysis of major elements at percent levels to very high accuracy and precision, including Si, Ca, Al, Fe, and S, and also minor elements such as Na, K, Ti, Mg, P, and Mn. The trace elements are also important for environmental pollution control, including species like Cr, Pb, Zn, Ni, As, Cd, V, and Cu at part-per-million levels.

Using the JY ULTIMA 2, researchers at Jobin Yvon ([www.jobinyvon.com](http://www.jobinyvon.com)) performed stability tests using a cement sample and measured Ca at the less sensitive 317.933-nm line because of the high concentrations in the solutions. The conditions used were 1200 W, plasma gas 14 L/min, and auxiliary gas 0.8 L/min.

A comparison was made with simultaneous and sequential internal standards. The results showed that in-run precision improved with the use of a simultaneous internal standard from 0.3% down to 0.15%, although the mean precision over 4 h was only 0.58% down to 0.50% RSD. This shows that although in-run precision can be improved, the ICP spectrometer is so stable that little improvement can be made. This was confirmed with results obtained with and without calibration over a five-day exercise (see Table 1).

**TABLE 2: Detection Limits in 10% NaOH and 10% NaCl**

Element	Wavelength (nm)	10% NaOH (µg/L)	10% NaCl (µg/L)
Al	396.152	5	5
As	189.042	5	2
B	208.959	1	1
Ba	455.403	0.1	0.1
Be	313.042	0.5	1
Ca	317.933	2	2
Cd	228.802	0.2	0.2
Co	228.616	0.2	0.2
Cr	267.716	0.5	0.5
Cu	324.754	1.3	1
Fe	259.940	0.3	0.3
K	766.490	5	5
Li	670.784	0.5	0.1
Mg	279.553	0.05	0.1
Mn	257.610	0.1	0.1
Mo	202.030	0.5	0.5
Ni	231.604	1	1
P	178.229	10	10
Pb	220.353	5	5
S	180.676	5	5
Sb	206.833	5	5
Se	196.090	5	10
Sr	407.771	0.1	0.1
Ti	334.941	0.3	0.4
Tl	190.864	5	10
V	292.402	2.5	2
Zn	213.856	0.2	0.5

Finally, detection limits were determined after running the blank 10 times. In this case, the blank samples were 10% NaOH and 10% NaCl (7). The detection limits are shown with the wavelengths used in Table 2.

### The Bottom Line

ICP spectrometers have the ability to analyze any sample, such as cements, in which there is a high salt content. However, depending on the plasma orientation and the quality of detection limits, accuracy and stability can be affected. Axial-view ICP instruments can be advantageous for simple matrices, such as clean samples where dissolved salts and matrix effects are often minimal. A radial-view ICP spectrometer, however, is recommended for more complex matrices or those with dissolved solids levels above 1%.

### References

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  - (7) Le Corre, N. *Analysis of 10% NaOH and 10% NaCl*; JY Application Note 01.
- (Note: JY application notes can be accessed at [www.jobinyvon.com](http://www.jobinyvon.com).)

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