



A Comparison of Radial and Axial View Plasma

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1 Introduction

The first paper describing axial ICP was published in the mid 1970's (1). However, many years passed before the first commercial ICP emerged in 1993, followed by another ICP about a year later. The latter became an instant success. The race had started for lower detection limits with claims of 10 times better detection limits for most elements using an axial ICP. But as the atomic spectroscopy community would find out, an axial plasma alone was not the singular solution for every sample.

2 Improvement in performance

It was soon discovered that axial plasma suffered from serious interferences caused mainly by ionization (2 - 3). Work on the special requirements of axial ICP was made to improve the performance. A primary need was to eliminate the fireball region of the plasma, while viewing just the central channel. Improved optical baffling was effective and produced the desired results for axial ICP. Improved optical baffling and better resolution improved performance with respect to noise for the radial ICPs as well, but for most spectrometers, this severely restricted the signal, so gains in detection limit were only small. Insufficient signal due to the optics has not led to the improvement in radial ICPs, except with the highest resolution ICP spectrometers with large optical components.

Recent work on high resolution, high optical efficiency ICP spectrometers have yielded improved detection limits with radial ICP of more than 10 times compared with low resolution ICP. The

results have led to detection limits on radial ICP better than published detection limits on axial ICP (4). The radial ICP system presented here is the JY ULTIMA 2 featuring a gigantic 110 x 110 mm grating, associated mirrors and a one-meter focal length monochromator.

Light throughput is a key parameter in the amount of signal and, hence, the detection limit. Modern master holographic gratings improve light throughput compared with ruled and replicate holographic gratings, these master holographic gratings also have reduced the amount of stray light. Stray light raises the background and thus increases noise and background equivalent concentration (BEC), which in turn has a direct effect on the detection limit. This is one of the limiting factors with solid state detector (SSD) spectrometers due to the need to use an Echelle optical system that has high stray light due in part to the use of very high orders (5).

Figure 1: Various regions of the plasma



Red = Initial Radiation Zone (IRZ)
 Blue = Normal Analytical zone (NAZ)
 Dark red = Molecular region of plasma





Optical coatings have also improved the optical efficiency, especially in the low UV region. Photomultiplier tube (PMT) designs have had some improvements mainly with respect to specialized requirements, e.g. solar blind PMT. The advantage of these particular PMTs is that they are blind above approximately 300 nm. This will minimize multiple order interferences if more than the first order is utilized. Some sequential ICPs use 2nd order light, or in some cases 3rd and 4th orders. The permutations of multiple order use may provide problems e.g. P at 178.29nm in steels if orders beyond the 2nd are used.

3 Axial viewed ICP

Axial ICPs can have improvement factors varying from 10 times down to 2-3 times compared with radial ICP, depending on the resolution of the spectrometer. The improvements in detection limit, may be useful for simple environmental applications, albeit for a modest increase in cost. However, radial ICPs have been shown to be more robust than axial ICPs. The Mg ion/atomic line test promoted by Mermet et al (6) is a good test of the "robustness" of the plasma system to various solutions that may present various interferences in the plasma. This is especially important where the solutions contain complex matrices as found in chemicals, metals, and geological samples.

The size of the Normal Analytical Zone (NAZ) viewed can affect the accuracy and, of course, recoveries obtained in any tests. Some spectrometers view a small region of the plasma, so that the viewing height becomes an important parameter to optimize. The NAZ (see figure 1) is above the bullet region or IRZ (Initial Radiation Zone). It is easy to avoid this region in radial ICP. However in axial ICPs it is viewed as well as increasing the path length of the NAZ. It is imperative in axial ICP to avoid the fireball region that surrounds the bullet and NAZ. This presents the engineers with the need to optically baffle the axial ICP more stringently, resulting in loss of light, to avoid excessive interferences. The more complex is the matrix, the larger is the problem. In organic analysis however, the organic

bullet cannot be avoided, the whole length of the organic bullet is viewed. This is why many elements may be worse on axial ICP compared with radial ICP, even on a comparable spectrometer, for organic solutions.

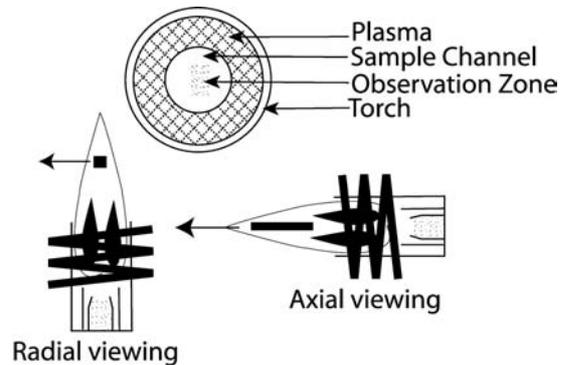


Figure 2: Cross section of the plasma and viewing regions of radial and axial plasma.

For axial ICPs the outer tube of the torch has to be longer to contain the plasma, this presents problems (as with ICP-MS) with dissolved solids. The salts attack the outer tube and can increase the consumable costs dramatically in some cases. For some samples 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 to create a curtain of gas, usually compressed air, to cut off viewing this region. Shear gas for elements below 190 nm requires nitrogen, an added cost. An alternative is to have a cone within the plasma similar to ICP-MS. The plasma is viewed without any contribution due to oxides and thus has better background and less interferences, plus the advantage of being able to determine elements in the low UV. However, there is an increase in argon consumption typically an extra 2.5 L/min.

Axial view gives more signal intensity due to the increased observation path length of the NAZ.



This leads to an improved detection limit by 2-3 times for high resolution increases in the axial view while background stays the same, so overall SBR increases and detection limits improve.

A limited aperture is required to view the Normal Analytical Zone (NAZ) channel, without including the fireball region of the plasma, however while the plasma tail can be eliminated by shear gas or a cone with an Argon counter flow gas, the bullet region observation cannot be avoided.

4 Radial ICP

Less matrix effects are found in radial ICP compared to axial viewing, due to the fact that the IRZ (or bullet region) is not viewed and can be avoided by choice of the viewing height. Less spectral interferences are found in radial viewing, especially organics, due to the reduction of band structures observed. No torch adjustment is required for each element if you view the entire Normal Analytical Zone (NAZ) and as the RF power and plasma gas are generally lower, any sample matrix can be run on radial ICP. Another advantage of the radial ICP is that due to the optical "thinness" of the radial plasma compared with the axial plasma, there is a wider linear dynamic range.

Less maintenance and less attention is required to the smaller radial torch than axial torch. The axial torch lifetime is severely degraded by dissolved salts and this can reduce torch lifetime, so radial torches last longer, especially with dissolved salts, reducing the running costs. Lower running costs are found with radial viewing, especially when argon consumption is taken into account, this is because there is a counter flow or shear gas required for axial viewing to eliminate the plasma tail. This is where all the recombination and oxides are found in the plasma and should be avoided at all costs.

5 Drawbacks of axial ICP

Axial view has more matrix interferences. In clean matrices the signal increases in the axial view while

the background stays similar, so the overall SBR increases and detection limits improve. However, in "difficult" matrices, the signal increase can be matched by an increase in the background, so the SBR can be the same or even worse, resulting in poor detection limits, especially for low UV e.g. Pb, Zn, As, Cd, P, Se and S. Because of the possibility of viewing the fireball region of the plasma, the slits and much optical baffling is required to reduce the high stray light. However, some systems have low efficiency optical systems, so the alignment of these axial systems is critical for both detection limit and interferences observed.

Axial ICP cannot eliminate viewing the bullet region of the plasma, this leads to high band structures being observed. Unlike radial viewing, one cannot optimize torch or plasma conditions to eliminate viewing the bullet. The obligatory observation of the bullet region produces high EIE (Easily Ionizable Element) effects. This makes the accurate determination of alkalis elements and other element affected by the EIE's difficult. Another effect of viewing the bullet region is that organics are poor by axial ICP due to various band structures raising the background and masking the analytical peaks. One method of reducing this effect is to utilize oxygen to minimize the band structures and prevent carbon buildup on the torch for the analysis of an organic solution.

6 What about dual view?

Is it the best of both plasma viewing worlds?

More recently dual view systems have been marketed using 3 mirrors. It should be noted that each mirror loses 5-10% signal as a compound loss. The design of these dual view systems must have one of the mirrors movable to be able to view either axial or radial. The movable mirror moves into position when radial view is required and out again when using axial view. Two separate runs must therefore be made to analyse the same sample if both major and trace elements are required using both plasma views.

In the design of the dual view system, one has to remember that it is optimized for axial view, hence



the torch is positioned in a horizontal plane. The torches used for dual view are longer to be able to use axial view. This means that problems such as reduced dissolved solids capability, of salt problems causing faster blockage and contamination around the torch add up to reduce the long term stability. The longer dual view torch also does not last as long and can have uneven vitrification on both outer and middle tubes, plus there is the possibility that the primary optics can be coated with sample debris.

7 Conclusion

Axial ICPs can be advantageous for simple matrices such as environmental samples where dissolved salts and matrix effects are often minimal. A radial ICP, however, is recommended for more complex matrices, especially organic samples. The JY ULTIMA 2 utilizes a radial plasma and yet still provides better detection limits than axial plasma systems. This is due in part to the high luminosity optics and excellent resolution of the ULTIMA 2.

8 References

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