

SmartNotes

How do I choose the right sample introduction system for my analysis?

QA

The selection of the sample introduction system depends on the sample matrix which will be analyzed.

For aqueous samples a general distinction can be made between samples with no dissolved solids or high dissolved solids or those that need high sensitivity.

When there are no or low dissolved solids, a simple sample introduction system with a concentric nebulizer and a cyclonic spray chamber is adequate. Aqueous solutions which contain up to 3% m/v total dissolved solids (TDS) can also be analyzed with a relatively basic sample introduction system, consisting of a concentric nebulizer and a single pass cyclonic spray chamber. This combination is very efficient at converting the liquid sample in to an aerosol and removing large droplets of solvent from the aerosol prior introduction to the plasma.



For samples containing more than 3% TDS a single pass cyclonic spray chamber, parallel path nebulizer and the use of an argon humidifier is recommended to prevent salt crystallization on the sample introduction parts.

High solid solutions containing up to 20% m/v TDS need a specific nebulizer which is designed not to block when aspirating high salt solutions. The spray chamber used will typically be a double pass which removes a greater proportion of the sample (when compared to the single pass described above). The use of this spray chamber serves at least two purposes, it prevents the plasma loading (the amount of sample entering the plasma) becoming too high, and, it also helps to prevent salt crystallization on the torch or center tube. Also, a large bore center tube should be used because this helps to reduce the risk of blockage. Additional accessories like the argon humidifier or the sheath gas adapter help to achieve long term stability.

When it comes to particles in solution, nebulizers can typically handle particle sizes of up to one third of the capillary diameter before blockage occurs.

When aiming for high sensitivity of some elements, an ultrasonic nebulizer or a hydride generator may be used to improve detection capability of the instrumentation.

For organic solutions such as, kerosene, xylene or toluene special solvent resistant pump tubing and sample introduction components are needed. A greater proportion of the sample pumped into the nebulizer is converted to an aerosol when compared to an aqueous solution. To prevent the plasma becoming unstable due to too much sample being transported to it, a less efficient sample introduction system must be used when analyzing organics, such a system would comprise a V-groove nebulizer and a double pass baffled cyclonic spray chamber. If the sample is very volatile the sample will need to be cooled prior to analysis, this is achieved by the use of a cooled spray chamber. There are several methods of cooling such as using a jacketed spray chamber or a peltier-cooled spray chamber. If the vapor pressure of the solution is greater than 4 kPa at room temperature a cool spray chamber will need to be used to achieve a stable plasma. Sample types which commonly require the use of a cooled spray chamber to analyze include petrol, benzene and naphtha.

Moreover, volatile organics can also be diluted with less volatile solvents, but one has to keep in mind that this also reduces detection sensitivity. Increasing the integration time can compensate the loss in sensitivity to some extent but it also increases analysis time.

For samples which contain hydrofluoric acid there are special sample introduction components which are made of materials which are resistant to hydrofluoric acid, these include PTFE spray chambers and nebulizers and ceramic torches.

Selection of a sample introduction system can be complex. However, the use of dedicated kits for specific applications simplifies the choice, limiting the options to a number of pre-optimized kits (Figure 1). The selection tool (Figure 2 & 3) also can aid, when deciding which sample introduction system to use.



Figure 1. Standard sample introduction kits for the Thermo™ Scientific™ iCAP™ 7000 Plus Series ICP-OES Duo, designed for the analysis of aqueous solutions containing up to 3% TDS.

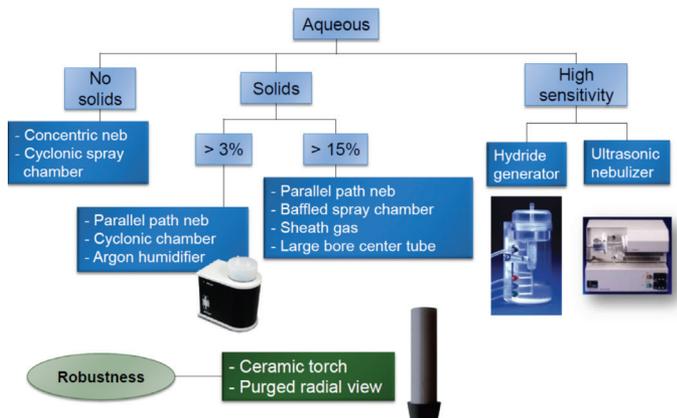


Figure 2. Aqueous sample introduction selection tool.

Relative intensity changes with increasing RF

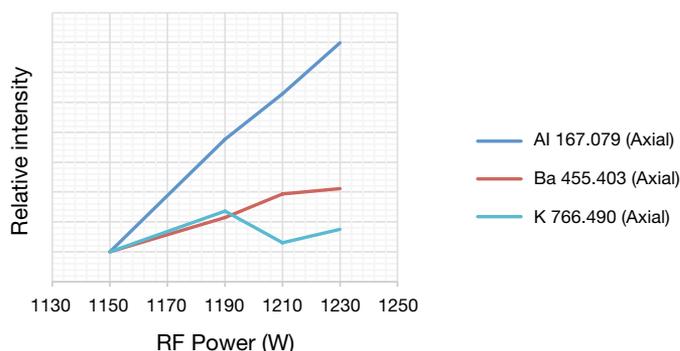


Figure 4. Relative intensity change with increasing RF power.

How to optimize plasma parameters?

• Nebulizer flow

Glass nebulizers are unique hand made parts, which means that each nebulizer has its own optimum gas flow. The Nebulizer flow effects wavelength below and above 220 nm differently (Figure 5), therefore a compromise has to be made and the standard parameters for aqueous samples are set to 0.5 L/min.

Nebulizer flow influence on intensity

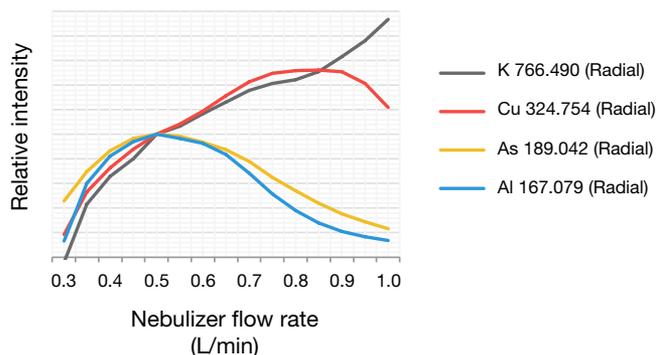


Figure 5. Nebulizer flow influence on intensity with aqueous solution.

• Sample flow rate

The sample flow rate is used to control the amount of sample entering the spray chamber and plasma. To keep a constant sample flow a peristaltic pump is recommended. The flow rate may have to be adapted to the nebulizer used. For aqueous samples usually a sample flow rate of 1.6 ml/min is used. For high matrix samples a lower sample flow rate of about 1.3 ml/min is recommended because less sample need to enter the plasma. Volatile samples need a even lower sample flow rate of about 0.7 ml/min.

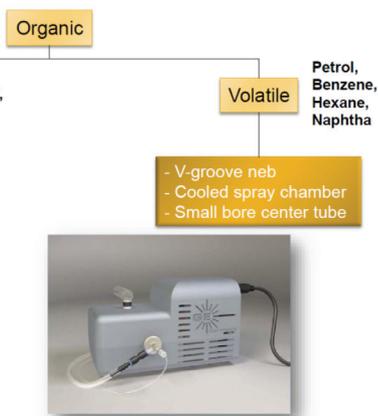


Figure 3. Organic sample introduction selection tool.

How do I know which RF power I should select?

Depending on the sample matrix and the wavelength selection, the RF power has to be adjusted. The Energy requirements of atomic and ionic wavelengths differ, ionic wavelengths require much more energy than atomic wavelengths. Most applications are multi-element analysis and for this a compromise of RF power as well as nebulizer flow has to be made.

Higher RF power effects ionic and atomic emission wavelengths with high excitation energy, so with wavelength below 250 nm like Aluminium, and results in an increase of intensities. Atomic wavelengths at 300 nm and higher like Barium are barely affected by the change of the RF power, whereas the sensitivity of Ionic wavelengths at 300 nm and higher like Potassium are negatively affected by increased RF power (Figure 4).

- **Auxiliary flow**

The auxiliary gas flow is used to elevate the bottom of the plasma away from the injector tube. The auxiliary flow is pertinent to high TDS and organic applications, which are prone to plasma loading. For this type of samples a higher auxiliary flow is used.

- **Cool Gas flow**

Between the outer tube and the auxiliary tube of a plasma torch, a tangential cool gas flow is introduced to contain the plasma and to keep it away from the outer torch tube because otherwise it would melt. The cool gas flow affects only certain matrices e.g. high salts and organics. The higher flows help to extend torch life time.

How do I know which view to use?

There are two views on the Duo view instrument, axial view and radial view. With the axial view the light from the plasma channel is detected, with this high sensitivity and good detection limits can be achieved but this view is also more affected by interferences. The radial view allows for a high linear dynamic range and better stability of the instrument but is also less sensitive.

How do I know which radial Viewing height to select?

The radial viewing height can only be adjusted on a radial only system. The viewing height is dependent on whether an atomic or ionic wavelength is observed. Atomic emission is taking place in the plasma core whereas ionic emission is taking place in the middle part of the plasma stream. So for ionic wavelengths a higher viewing height is selected then for atomic wavelengths.

What do I have to consider when selecting the integration time?

The integration or also called exposure time is the time the instrument will be detecting signals. When measuring high concentrations you have to consider that saturation can happen. When measuring lower concentrations the integration time can be extended to achieve better detection limits.

How do I select the correct wavelength?

Considerations for the selections of the correct wavelength are the sample matrix, possible interferences from other elements, the linear range required and that the wavelength has sufficient sensitivity.

Ideally the matrix should match with all samples and standards. If this is not possible at least the acid concentration should match.

To overcome Matrix effects the correct use of the background correction is important. Dilution usually helps to reduce the effect of the matrix, an internal standard (IS) can correct the effect of a matrix and the use of standard addition can also be considered.

The matrix of a sample can lead to different interferences in an ICP-OES method. There are physical, chemical and spectral interferences.

- Physical interferences can be described as: A characteristic difference between sample and standard which affects sample introduction or nebulization.

Causes can be:

- Viscosity
- Density
- Surface tension

Solutions are:

- Dilution of the sample
- Matrix matching
- Internal standardization
- Method of standard addition

- Chemical interferences can be described as: A sample matrix characteristic which causes an analyte to behave differently in the sample and standard.

Causes can be:

- Ionization
- Molecule formation
- Plasma loading

Solutions are:

- Dilution of the sample
- Use of ionization buffer
- Oxygen addition for organic samples
- Plasma optimization
- Matrix matching
- Internal standardization

- Spectral interferences are those that are most dealt with in ICP-OES. These type of interferences can be really severe.

There are different kind of spectral interferences:

- Background shift that come from matrix
- Nearby interferences from other elements in the sample
- Direct spectral overlap that occur when two analytic wavelength are so close together that they cannot be resolved

To correct for this an off- peak background correction (Figure 6) and sometimes also an inter-element correction is needed. Viewing the Fullframes (Figure 7), which are visualized intensity distribution on the photo detector, can provide insight on spectral interferences coming from other orders of the spectrum.

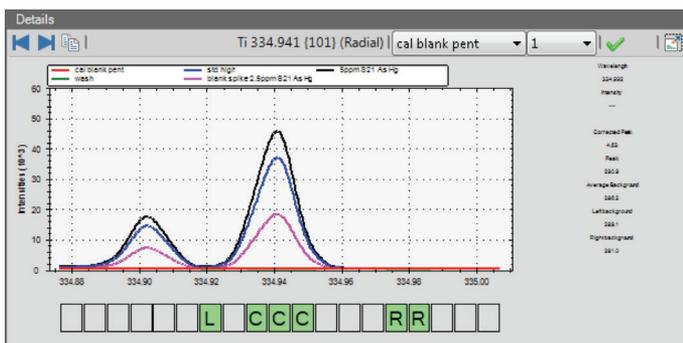


Figure 6. Subarray of an element with Thermo Scientific iCAP 7000 plus series ICP-OES software .

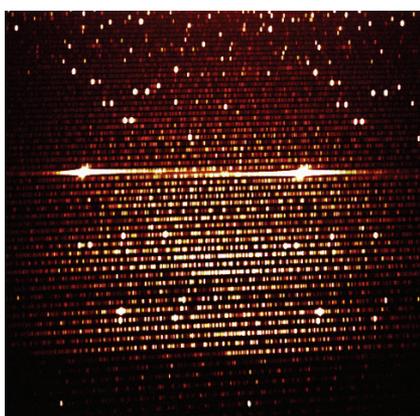


Figure 7. Fullframe of a spectrum with the Thermo Scientific iCAP 7000 plus series ICP-OES.

The Linear range is often set by regulations or protocols, EPA 200.7 is one example.

Determine the linear range of an element can be done by continually increasing the concentration of the highest standard by 10% and then read this back as an unknown sample. If this concentration is still in range, it can be added to the calibration curve. This process can be continued until the response is no longer linear.

Are there tools to make method development easier?

Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software for the iCAP 7000 plus series has an integrated method development tool consisting of two parts, the Element Finder plug-in and the Plasma Optimization.

Plasma Optimization optimizes the RF power and nebulizer flow based on the sample type which can be aqueous or organic. Plasma optimization can be performed for intensity, signal to background ratio or signal to square root of background ratio.

The Element Finder plug-in identifies wavelength suitable for the analysis based on the sample, this is done either manual or by automated selection of analyte and matrix elements.

With the Element Finder plug-in wavelength selection is done in just three easy steps. In the first step the sample is analyzed using a Fullframe, therefore only the sample type has to be selected which is either aqueous or organic. The second step will show which elements were found and will suggest a wavelength to use, a manual selection of preferred wavelength is also possible. Interferences will be shown in the subarray window to improve the selection. In the third and final step the results are imported in a LabBook and can be used for measurement. This process takes less than 5 minutes and only 8 ml of sample solution.

Both, the Element Finder and the Plasma Optimization can be performed with manual sampling or using an autosampler.

What do I have to consider for the method validation?

- **Quality Control (QC)**

Are used to ensure that your method is running reliably and the data generated is valid.

- **Blank test**

The blank test helps to decide whether there is a contamination or carryover from an previous sample.

- **Recovery test**

Can be used to check if the calibration is still valid. With this the known concentration is analyzed and the percentage recovery is recalculated.

- **Spike test**

Spike tests give an indication about the recovery of spiked sample concentration, this gives an idea about possible differences between calibration and sample, that for example caused by interferences.

- **Internal standard**

Internal standards are dynamic drift corrections used to correct for physical differences in samples and standards by referencing all samples to the same element performance. A correction is then applied to the sample in accordance with the suppression or enhancement of signal experienced by the IS element. Internal standards must be referenced to elements that will react the same way in the plasma, i.e. they are all UV, or all ionic wavelengths. An element wavelength and its internal standard wavelength should have the same plasma view and slit i.e. Axial/Axial, and Radial/Radial and UV/UV and VIS/VIS. The wavelength of the IS must be interference free, the background correction must be used and the IS must be added precisely to all samples. To add the internal standard an internal standard mixing kit can be used duo to the online addition of the standard.

Conclusion

The choice of the right sample introduction system and the selection of the right plasma and method parameters are important. Certain features like internal standard, inter-element correction and quality control help to facilitate method development. Physical, chemical and spectral interferences have to be considered when selecting wavelength. With the Thermo Scientific Qtegra (ISDS) software integrated Element Finder plug-in and the Plasma Optimization, the selection of wavelength and plasma parameters can be automated. With the Element Finder plug-in, method development can be performed in just 3 simple steps, in less than 5 min and with only 8 ml of sample.

Find out more at thermofisher.com/ICP-OES

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