

# Sector-Field ICP-MS

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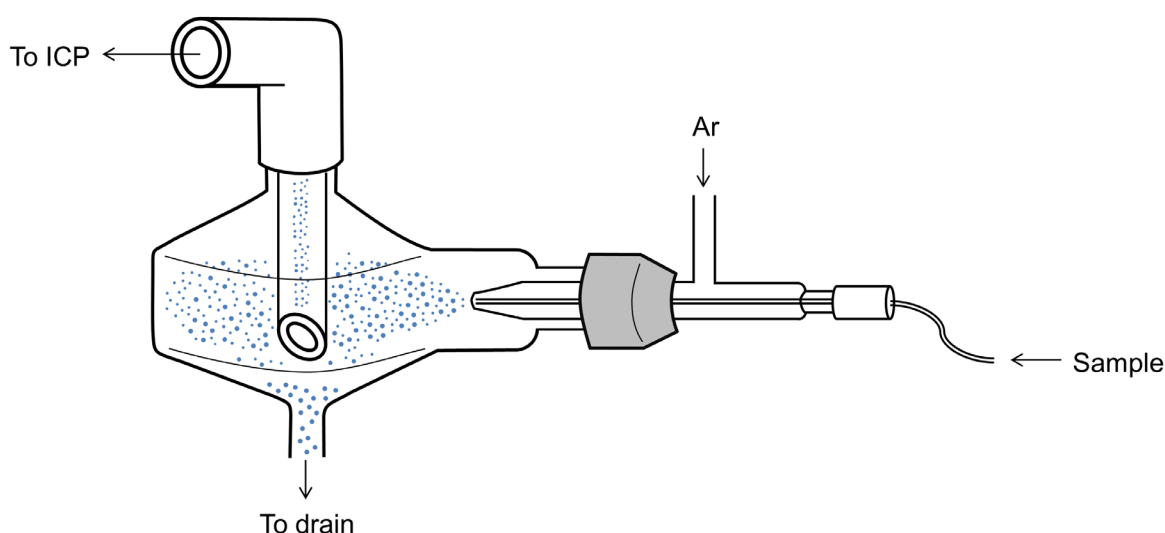
Inductively coupled plasma mass spectrometry (ICP-MS) is capable of detecting most elements in the periodic table. The technique offers many advantages for the analysis of elements, including high sensitivity, a large linear dynamic range and the ability to provide isotopic information. Quantification can be accomplished by comparison with internal or external calibration standards. However, for certain isotopes, the presence of interferences can produce results that are not representative of the sample. This simulation includes the analysis of several elements that suffer from interference.

## How does the ICP-MS work?

An ICP-MS instrument consists of 4 main components; the sample introduction system, the ionisation source, the mass analyser, and the detector.

### Sample introduction

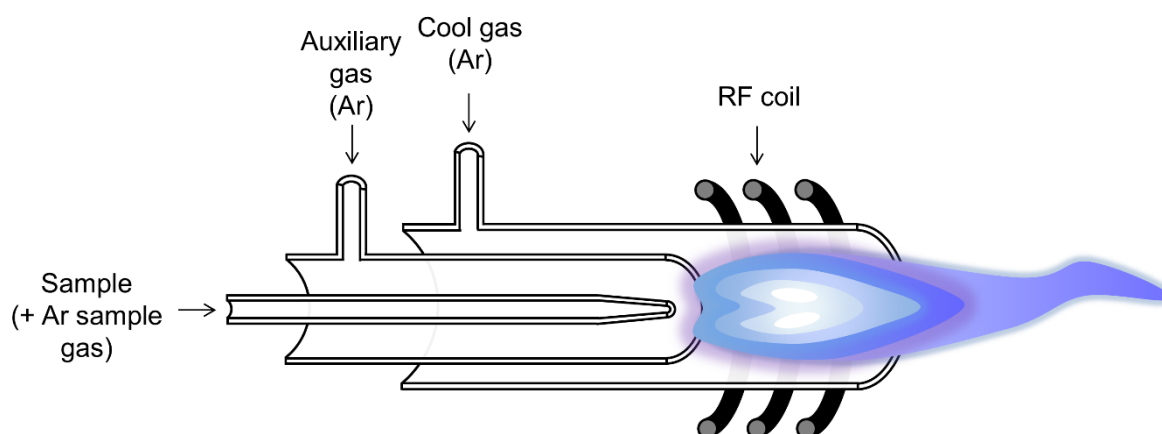
Most ICP-MS analyses involve the introduction of samples in liquid form. Sample solutions are taken up by narrow tube, called a probe, and passed through a nebuliser, which generates polydisperse sample droplets. A spray chamber is used to remove the larger droplets before the sample enters the ICP. *Note that direct analysis of solids is also possible e.g. by using laser ablation, but this simulation focusses on the analysis of solutions only.*



**Figure 1.** A diagram of the concentric nebuliser and cyclonic spray chamber used to introduce samples in this simulation. Nebulised sample droplets are shown in blue.

## Ionisation

The ICP is a high temperature (>6000 K) ionisation source that atomises the sample and converts it into positively charged ions. It is considered a hard ionisation source because after material has passed through the ICP information on its molecular structure is lost.



**Figure 2.** Cut-through schematic of an ICP torch, showing three concentric quartz tubes with argon gas flows. A radiofrequency field in the top section of the torch sustains the plasma.

## Mass analysis

Ions are focussed towards the mass analyser using a series of lenses. A variety of options are available to separate ions, including quadrupole and time of flight mass analysers. However, this simulation is based on the Thermo Element XR, a type of double focussing sector-field instrument that uses a magnetic and an electrostatic analyser.

In the magnetic sector, the ions are dispersed by their energy and momentum, where the momentum of an ion is its mass multiplied by its velocity. At a given magnetic field strength, the radius of the trajectory through the magnetic field is dependent on the momentum and charge of the ion. Hence, for ions of a uniform velocity, the strength of the magnetic field can be adjusted to allow ions of the desired mass/charge ( $m/z$ ) to pass through the magnetic sector (BScan mode). Similarly, when the magnetic field is held constant, varying the acceleration voltage, and hence the velocity of the ions, also provides mass separation (EScan mode).

Ions exiting the magnetic sector have slight variation in energies, related to their point of formation in the ICP. For single focussing instruments, this energy spread may cause broadening of peaks and loss of resolution. Therefore, an electrostatic analyser, which is dispersive with respect to ion energy, is included (see Figure 3). This combined usage of magnetic and electrostatic sectors is referred to as double focussing.

## Detection

Ions exiting the mass analyser are focussed onto the detector, producing signals that are proportional to ion abundance. This simulated instrument uses two detectors, a secondary electron multiplier (SEM) and a Faraday detector. The SEM may be operated in either counting mode, for amplification of trace signals ( $<5 \times 10^6$  cps), or in analog mode, for mid-range signals. The Faraday detector is reserved for very high signals, above  $1 \times 10^9$  cps. In the default setting of 'Triple mode', the instrument automatically switches to the appropriate detector depending on the count rate.

## Method vs. Manual Scan

Users may choose to perform either a method or a manual scan. The manual scan enables the user to perform a rapid scan over a specified continuous mass range. This is helpful for initial qualitative analysis of an unknown sample, to see what is there. However, limited time is spent focussing on the tops of each peak, so this option is rarely used for quantitative analysis. The alternative option, method scan, focuses solely on isotopes that are specified within a method file. The instrument will switch between measuring each selected isotope in turn, performing multiple scans across the top of each peak for the time duration specified in the method. *Note that users may observe a slight difference in the count rates obtained using the method vs. manual scan mode, due to the differing acquisition and data evaluation parameters used.*

## Spectral Interferences

When performing a manual scan of the mass range, users will notice that the mass spectrum is dominated by a few very large peaks. These relate to argon-based interferences. The ICP is generated using an argon gas, thus large amounts of argon are present in the interface of the mass spectrometer. In the high temperature environment, molecular ions may form that would not be stable under normal laboratory conditions. For example, argon may combine with itself to form an argon dimer or it may combine with other atmospheric or matrix components to form ArH, ArC, ArN, ArO, ArCl etc. This poses problems if the  $m/z$  of the molecular ions overlap with any isotopes of interest. Two examples of elements that are impacted by molecular ion interferences are Fe and Se, as shown in Tables 1 and 2.

In addition to molecular ion interference, doubly charged ions may form for elements that are easily ionised. An example is barium, which may form  $^{138}\text{Ba}^{2+}$ , producing a peak that may interfere with  $^{69}\text{Ga}^+$  in the mass spectrum. Isobaric interference, where one or more isotopes have nominally identical  $m/z$  values, is also common. Examples of isobaric interference include  $^{48}\text{Ti}$  on  $^{48}\text{Ca}$  and  $^{54}\text{Cr}$  on  $^{54}\text{Fe}$ .

**Table 1.** Examples of argon related interferences affecting iron analysis. The relative abundances of the iron isotopes are shown in brackets.

Fe isotope	Interference
<sup>54</sup> Fe (5.8%)	<sup>40</sup> Ar <sup>14</sup> N
<sup>56</sup> Fe (91.7%)	<sup>40</sup> Ar <sup>16</sup> O
<sup>57</sup> Fe (2.2%)	<sup>40</sup> Ar <sup>16</sup> O <sup>1</sup> H
<sup>58</sup> Fe (0.3%)	<sup>40</sup> Ar <sup>18</sup> O

**Table 2.** Examples of argon related interferences affecting selenium analysis. The relative abundances of the selenium isotopes and their interferences are shown in brackets.

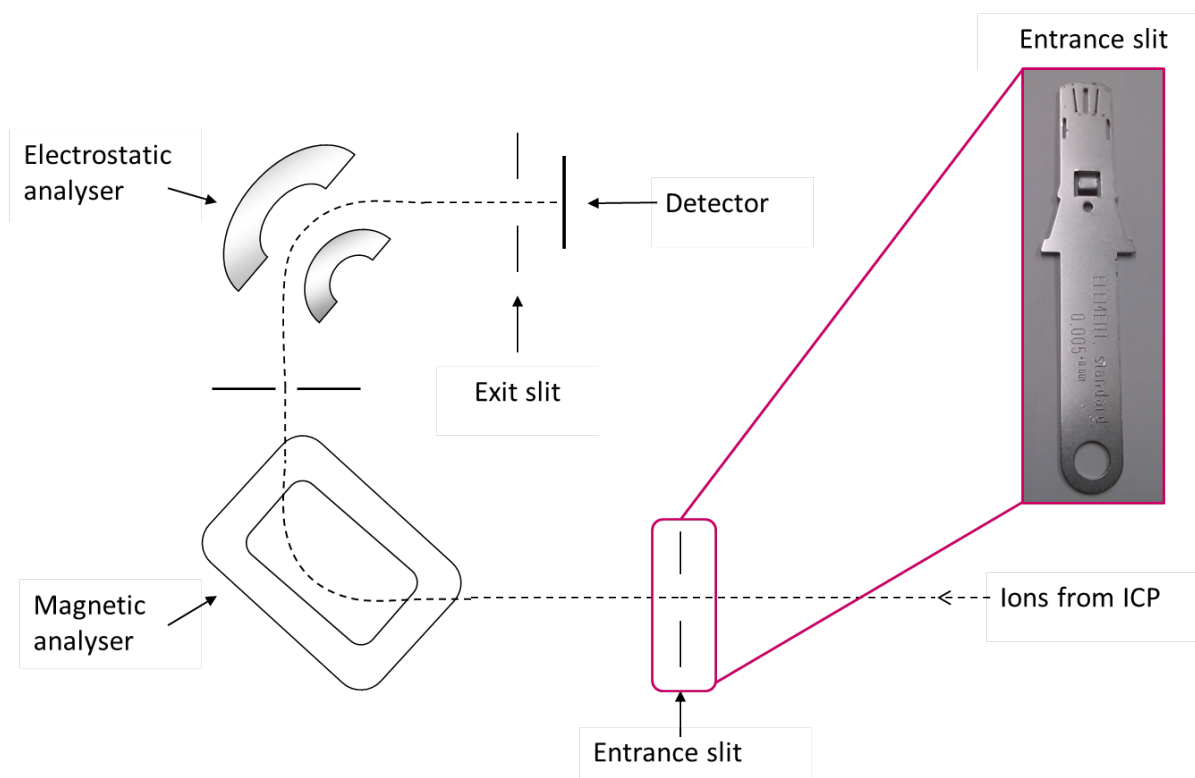
Se isotope	Interference
<sup>74</sup> Se (0.9%)	<sup>36</sup> Ar <sup>38</sup> Ar (0.0004%)
<sup>76</sup> Se (9.4%)	<sup>36</sup> Ar <sup>40</sup> Ar (0.67%)
<sup>77</sup> Se (7.6%)	<sup>40</sup> Ar <sup>37</sup> Cl (24.1%)
<sup>78</sup> Se (23.8%)	<sup>38</sup> Ar <sup>40</sup> Ar (0.13%)
<sup>80</sup> Se (49.6%)	<sup>40</sup> Ar <sup>40</sup> Ar (99.2%)
<sup>82</sup> Se (8.7%)	<sup>82</sup> Kr (11.6%)*

\* isobaric interference from <sup>82</sup>Kr, often present as an impurity in the argon gas

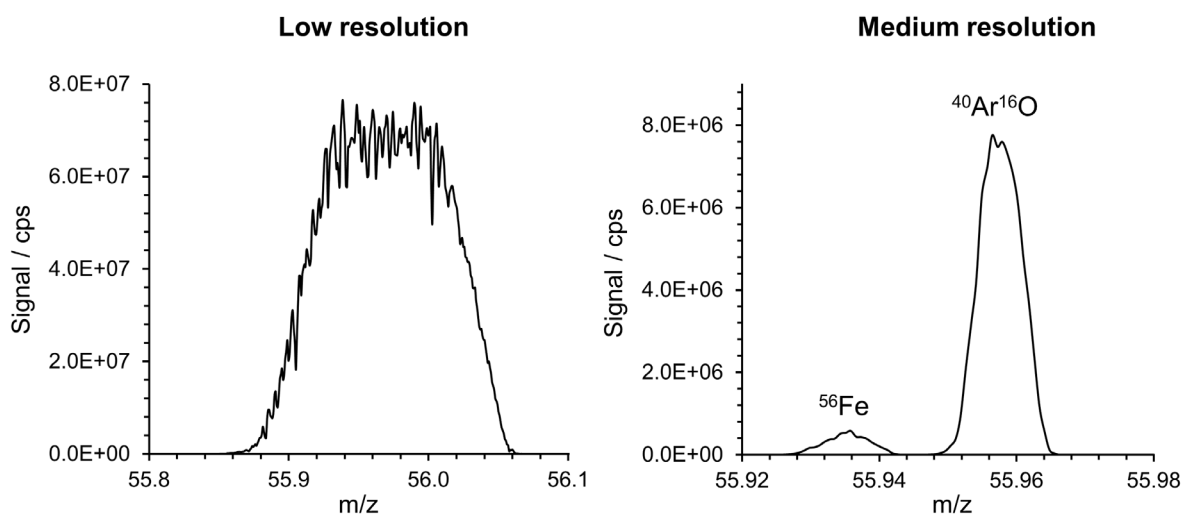
## Reducing Spectral Interferences

This simulation is based upon the Thermo Element XR, which is equipped with three mass resolution modes; low ( $R = 300$ , for non-interfered isotopes), medium ( $R = 4000$ , for easily resolved interferences) and high ( $R = 10000$  for more challenging interferences). Here, resolution ( $R$ ) is defined as  $M/\Delta M$ , where  $M$  is the mass number and  $\Delta M$  is the difference in mass between the two neighbouring peaks.

The instrument can be switched between the three modes by adjusting the width of the entrance and exit slits, positioned either side of the mass analysers (see Figure 3). A narrower slit will increase the mass resolution and help to resolve spectral interferences, but this improvement comes at the expense of sensitivity because fewer ions are transmitted. The impact of this is shown for iron analysis in Figure 4. The shape of the peak also changes depending on sensitivity, with flat topped peaks observed for low resolution, compared to triangular shaped peaks for medium and high-resolution modes.



**Figure 3.** A schematic of the Thermo Element XR, showing the position of the entrance and exit slits. The top part of each slit plate has three rectangular apertures corresponding to low (middle), medium (left) and high (right) mass resolution modes.



**Figure 4.** A small section of the mass spectrum showing a comparison of  $^{56}\text{Fe}$  measurement using low and medium mass resolution settings. Medium resolution mode enables the  $^{56}\text{Fe}$  peak to be resolved from the argon oxide interference.

## Non-spectral Interferences

In addition to spectral interferences, other difficulties may arise from components present in the sample matrix. This could potentially lead to artificial suppression or enhancement of the sample relative to the standards. For example, the presence of carbon (ionisation potential of 11.3) is known to increase ionisation for some elements that have lower ionisation potentials. A contrasting example is sodium (ionisation potential of 5.1), which if present in large amounts may suppress ionisation of elements that have higher ionisation potentials. The simplest way to correct for these issues is to ensure that the samples and standards are matrix matched. Inclusion of an internal standard is also recommended to account for any changes to the efficiency of the nebuliser or ICP-MS during the run.