

A Beginner's Guide to ICP-MS

Part V: The Ion Focusing System

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Part V of the series on inductively coupled plasma–mass spectrometry (ICP-MS) takes a detailed look at the ion focusing system — a crucial area of the ICP mass spectrometer where the ion beam is focused before it enters the mass analyzer. Sometimes known as the ion optics, it comprises one or more ion lens components, which electrostatically steer the analyte ions from the interface region into the mass separation device. The strength of a well-designed ion focusing system is its ability to produce low background levels, good detection limits, and stable signals in real-world sample matrices.

Although the detection capability of ICP-MS is generally recognized as being superior to any of the other atomic spectroscopic techniques, it is probably most susceptible to the sample's matrix components. The inherent problem lies in the fact that ICP-MS is relatively inefficient; out of every million ions generated in the plasma, only one actually reaches the detector. One of the main contributing factors to the low efficiency is the higher concentration of matrix elements compared with the analyte, which has the effect of defocusing the ions and altering the transmission characteristics of the ion beam. This is sometimes referred to as a space charge effect, and it can be particularly severe when the matrix ions have a heavier mass than the analyte ions (1). The role of the ion focusing system is therefore to transport the maximum number of analyte ions from the interface region to the mass separation device, while rejecting as many of the matrix components and non-analyte-based species as possible. Let us now discuss this process in greater detail.

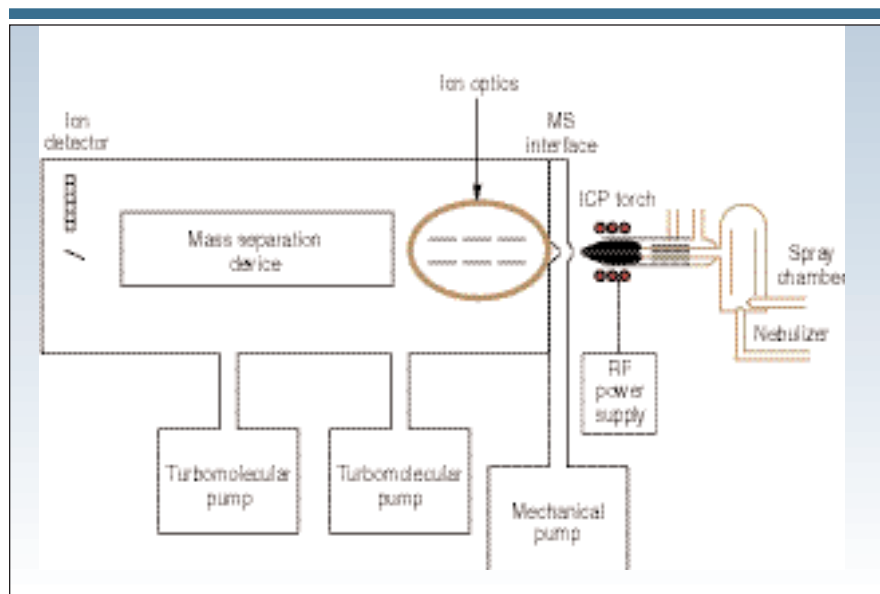


Figure 1. Position of ion optics relative to the plasma torch and interface region.

ROLE OF THE ION OPTICS

Figure 1 shows the position of the ion optics relative to the plasma torch and interface region; Figure 2 represents a more detailed look at a typical ion focusing system.

The ion optics are positioned between the skimmer cone and the mass separation device, and consist of one or more electrostatically controlled lens components. They are not traditional optics that we associate with ICP emission or atomic absorption but are made up of a series of metallic plates, barrels, or cylinders that have a voltage placed on them. The function of the ion optic system is to take ions from the hostile environment of the plasma at atmospheric pressure via the interface cones and steer them into the mass analyzer, which is under high vacuum. As mentioned in Part IV of the series, the plasma discharge, interface region, and ion optics have to be designed

in concert with each other. It is absolutely critical that the composition and electrical integrity of the ion beam is maintained as it enters the ion optics. For this reason it is essential that the plasma is at zero potential to ensure that the magnitude and spread of ion energies are as low as possible (2).

A secondary but also very important role of the ion optic system is to stop particulates, neutral species, and photons from getting through to the mass analyzer and the detector. These species cause signal instability and contribute to background levels, which ultimately affect the performance of the system. For example, if photons or neutral species reach the detector, they will elevate the background noise and therefore degrade detection capability. In addition, if particulates from the matrix penetrate farther into the mass spectrometer region, they have the potential to deposit on lens com-

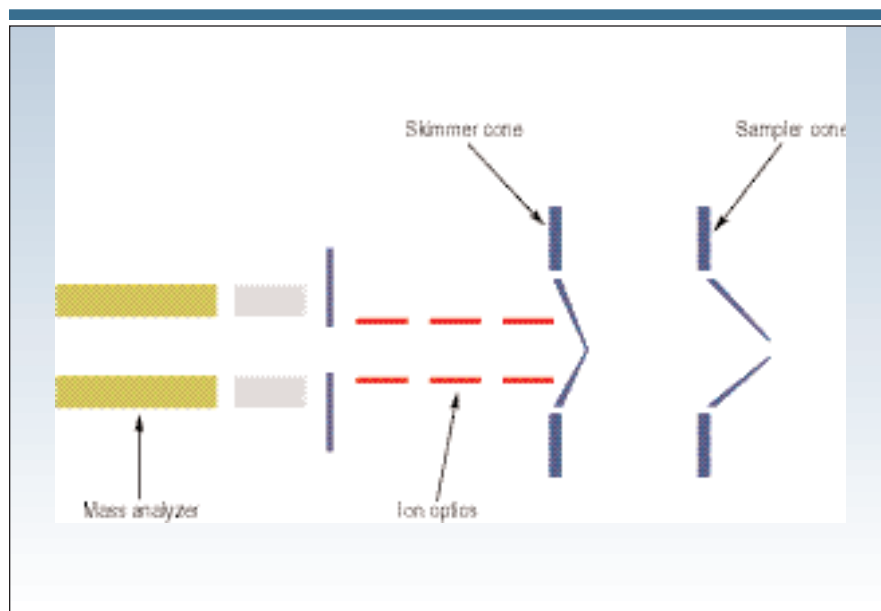


Figure 2. A generic ion focusing system, showing position of ion optics relative to the interface cones and mass analyzer.

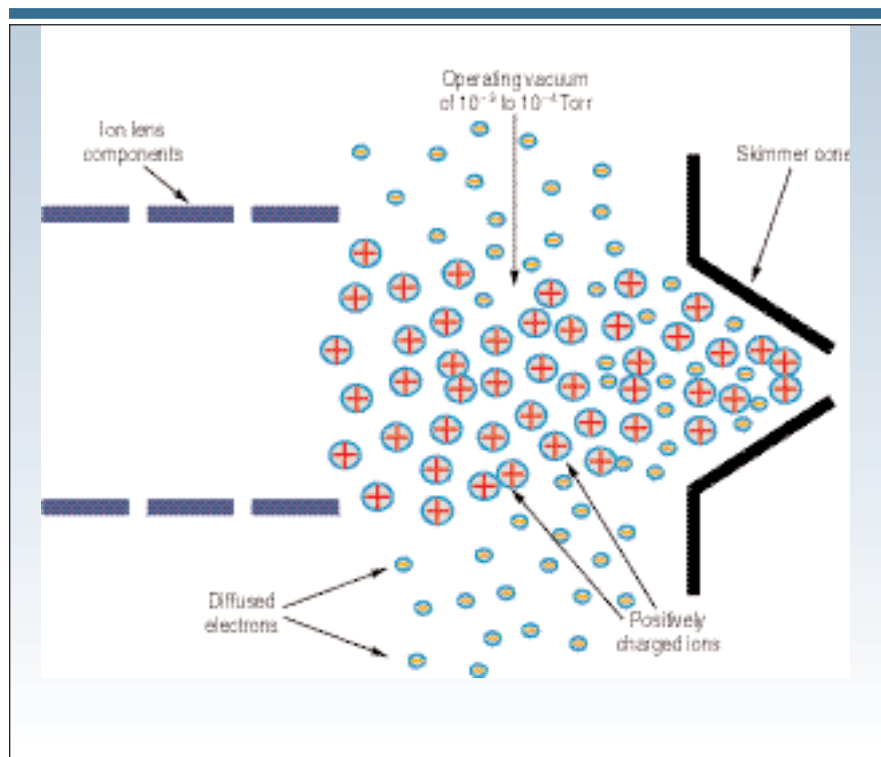


Figure 3. Extreme pressure drop in the ion optic chamber produces diffusion of electrons, resulting in a positively charged ion beam.

ponents and, in extreme cases, get into the mass analyzer. In the short term this will cause signal instability and, in the long term, increase the frequency of cleaning and routine maintenance.

Basically two approaches will reduce the chances of these undesirable species

making it into the mass spectrometer. The first method is to place a grounded metal stop (disk) behind the skimmer cone. This stop allows the ion beam to move around it but physically blocks the particulates, photons, and neutral species from traveling downstream (3). The other

approach is to set the ion lens or mass analyzer slightly off axis. The positively charged ions are then steered by the lens system into the mass analyzer, while the photons and neutral and nonionic species are ejected out of the ion beam (4).

It is also worth mentioning that some lens systems incorporate an extraction lens after the skimmer cone to electrostatically pull the ions from the interface region. This has the benefit of improving the transmission and detection limits of the low-mass elements (which tend to be pushed out of the ion beam by the heavier elements), resulting in a more uniform response across the full mass range of 0–300 amu. In an attempt to reduce these space charge effects, some older designs have used lens components to accelerate the ions downstream. Unfortunately this can have the effect of degrading the resolving power and abundance sensitivity (ability to differentiate an analyte peak from the wing of an interference) of the instrument because of the much higher kinetic energy of the accelerated ions as they enter the mass analyzer (5).

DYNAMICS OF ION FLOW

To fully understand the role of the ion optics in ICP-MS, it is important to have an appreciation of the dynamics of ion flow from the plasma through the interface region into the mass spectrometer. When the ions generated in the plasma emerge from the skimmer cone, there is a rapid expansion of the ion beam as the pressure is reduced from 760 Torr (atmospheric pressure) to approximately 10^{-3} to 10^{-4} Torr in the lens chamber with a turbomolecular pump. The composition of the ion beam immediately behind the cone is the same as the composition in front of the cone because the expansion at this stage is controlled by normal gas dynamics and not by electrostatics. One of the main reasons for this is that, in the ion sampling process, the Debye length (the distance over which ions exert influence on each other) is small compared with the orifice diameter of the sampler or skimmer cone. Consequently there is little electrical interaction between the ion beam and the cone and relatively little interaction between the individual ions in the beam. In this way, compositional integrity of the ion beam is maintained throughout the interface region (6). With this rapid drop in pressure in the lens chamber, electrons diffuse out

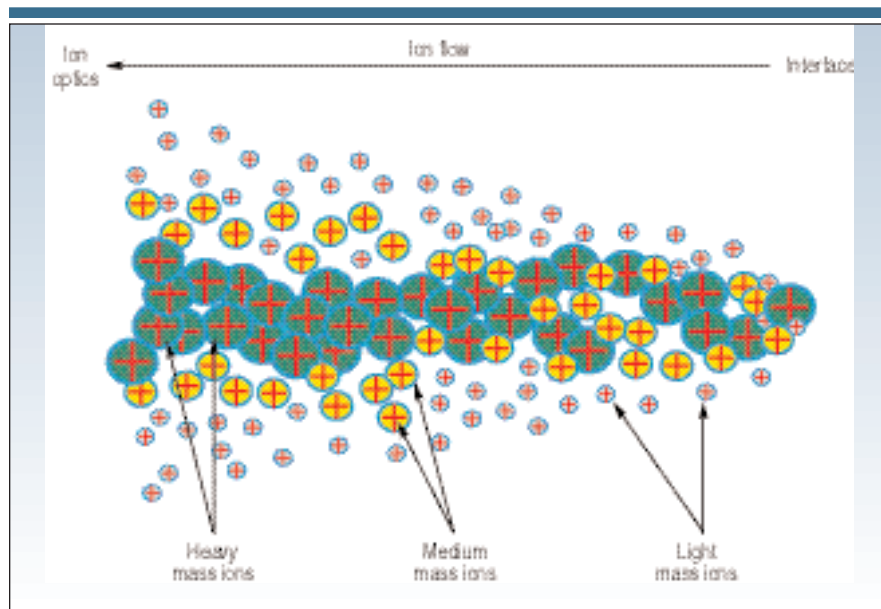


Figure 4. The degree of ion repulsion will depend on kinetic energy of the ions: those with high kinetic energy (green with red +) will be transmitted in preference to ions with medium (yellow with red +) or low kinetic energy (blue with red +).

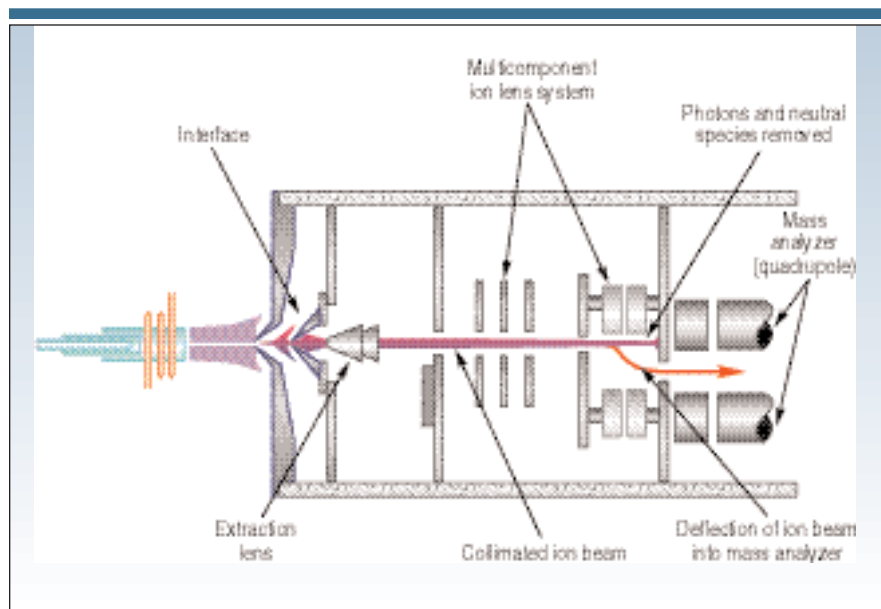


Figure 5. Schematic of a multicomponent lens system with extraction lens and off-axis quadrupole mass analyzer (courtesy of Agilent Technologies [Wilmington, DE]).

of the ion beam. Because of the small size of the electrons relative to the positively charged ions, the electrons diffuse farther from the beam than the ions, resulting in an ion beam with a net positive charge. This is represented schematically in Figure 3.

The generation of a positively charged ion beam is the first stage in the charge separation process. Unfortunately, the net

positive charge of the ion beam means that there is now a natural tendency for the ions to repel each other. If nothing is done to compensate for this, ions with a higher mass-to-charge ratio will dominate the center of the ion beam and force the lighter ions to the outside. The degree of loss will depend on the kinetic energy of the ions: those with high kinetic energy (high mass elements) will be transmitted

in preference to ions with medium (mid-mass elements) or low kinetic energy (low-mass elements). This is shown in Figure 4. The second stage of charge separation is therefore to electrostatically steer the ions of interest back into the center of the ion beam by placing voltages on one or more ion lens components. Remember, however, that this is possible only if the interface is kept at zero potential, which ensures a neutral gas-dynamic flow through the interface and maintains the compositional integrity of the ion beam. It also guarantees that the average ion energy and energy spread of each ion entering the lens systems are at levels optimum for mass separation. If the interface region is not grounded correctly, stray capacitance will generate a discharge between the plasma and sampler cone and increase the kinetic energy of the ion beam, making it very difficult to optimize the ion lens system (7).

COMMERCIAL ION OPTIC DESIGNS

Over the years, there have been many different ion optic designs. Although they all have their own characteristics, they perform the same basic function: to discriminate undesirable matrix- or solvent-based ions so that only the analyte ions are transmitted to the mass analyzer. The most common ion optics design used today consists of several lens components, which all have a specific role to play in the transmission of the analyte ions (8). With these multicomponent lens systems, the voltage can be optimized on every lens of the ion optics to achieve the desired ion specificity. Over the years this type of lens configuration has proven to be very durable and has been shown to produce very low background levels, particularly when combined with an off-axis mass analyzer. However, because of the interactive nature of parameters that affect the signal response, the more complex the lens system the more variables have to be optimized, particularly if many different sample types are being analyzed. This isn't such a major problem because the lens voltages are all computer-controlled, and methods can be stored for every new sample scenario. Figure 5 is a commercially available multicomponent lens system, with an extraction lens and off-axis quadrupole mass analyzer, showing how the ion beam is deflected into the mass analyzer, while the photons and

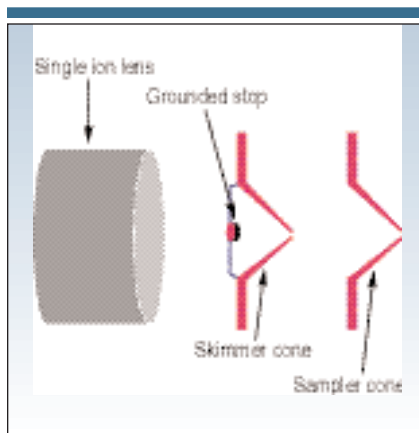


Figure 6. Schematic of a single ion lens and grounded stop system (not to scale [courtesy of PerkinElmer Instruments {Norwalk, CT}]).

neutral species travel in a straight line and strike a metal plate.

Another, more novel approach is to use just one cylindrical ion lens, combined with a grounded stop positioned just inside the skimmer cone as shown in Figure 6 (9).

With this design, the voltage is dynamically ramped on-the-fly, in concert with the mass scan of the analyzer (typically a quadrupole). The benefit of this approach is that the optimum lens voltage is placed on every mass in a multielement run to allow the maximum number of analyte ions through, while keeping the matrix ions to an absolute minimum. This is represented in Figure 7, which shows a lens voltage scan of six elements: lithium, cobalt, yttrium, indium, lead, and uranium, at 7, 59, 89, 115, 208, and 238 amu, respectively. We can see that each element has its own optimum value, which is then used to calibrate the system, so the lens can be ramp-scanned across the full mass range. This type of approach is typically used in conjunction with a grounded stop to act as a physical barrier to reduce particulates, neutral species, and photons from reaching the mass analyzer and detector. Although this design produces slightly higher background levels, it offers excellent long-term stability with real-world samples. It works well for many sample types but is most effective when low mass elements are being determined in the presence of high-mass-matrix elements.

It is also worth emphasizing that a number of ICP-MS systems offer what is known as a *high-sensitivity interface*.

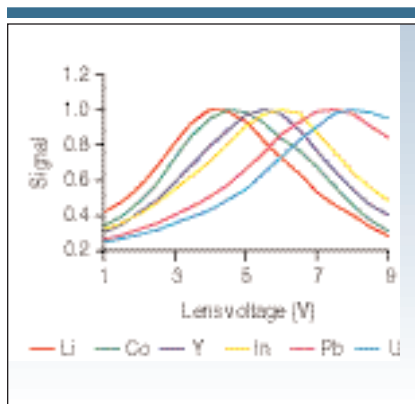


Figure 7. A calibration of optimum lens voltages is used to ramp-scan the ion lens in concert with the mass scan of the analyzer. The signals have been normalized for comparison purposes.

These all work slightly differently but share similar components. By using a combination of slightly different cone geometry, higher vacuum at the interface, one or more extraction lenses, and slightly modified ion optic design, they offer as much as 10 times the sensitivity of a traditional interface (10). However, this increased sensitivity is usually combined with inferior stability and an increase in background levels, particularly for samples with a heavy matrix. To get around this degradation in performance one must usually dilute the samples before analysis, which limits the systems' applicability for real-world samples (11). However, they have found a use in non-liquid-based applications in which high sensitivity is crucial, for example in the analysis of small spots on the surface of a geological specimen using laser ablation ICP-MS. For this application, the instrument must offer high sensitivity because a single laser pulse is used to ablate the sample and sweep a tiny amount of the dry sample aerosol into the ICP-MS (12).

The role of the ion focusing system cannot be overestimated. It affects the background noise level of the instrument. It has a huge impact on both long- and short-term signal stability, especially in real-world samples, and it also dictates the number of ions that find their way to the mass analyzer. However, it must be emphasized that the ion optics are only as good as the ions that feed it, and for this reason it must be designed in concert with both the plasma source and the interface region. There is no question that this area is crucial to the design of the whole ICP mass spectrometer. In the

next part of the series we will discuss the heart of the ICP mass spectrometer: the mass analyzer.

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