

# A Beginner's Guide to ICP-MS

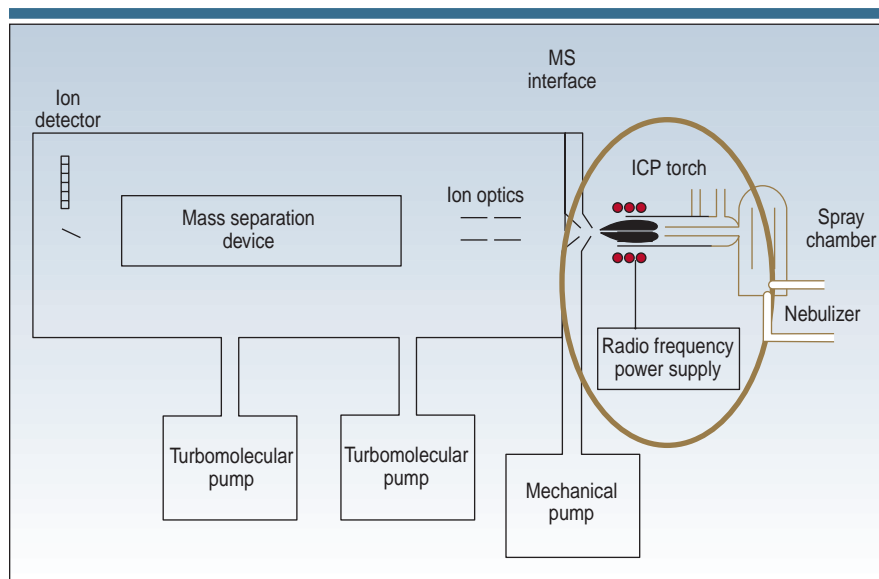
## Part III: The Plasma Source

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Part III of Robert Thomas' series on inductively coupled plasma-mass spectroscopy (ICP-MS) looks at the area where the ions are generated — the plasma discharge. He gives a brief historical perspective of some of the common analytical plasmas used over the years and discusses the components that are used to create the ICP. He finishes by explaining the fundamental principles of formation of a plasma discharge and how it is used to convert the sample aerosol into a stream of positively charged ions.

Inductively coupled plasmas are by far the most common type of plasma sources used in today's commercial ICP-optical emission spectrometry (OES) and ICP-MS instrumentation.

However, it wasn't always that way. In the early days, when researchers were attempting to find the ideal plasma source to use for spectrometric studies, it was unclear which approach would prove to be the most successful. In addition to ICPs, some of the other novel plasma sources developed were direct current plasmas (DCP) and microwave-induced plasmas (MIP). A DCP is formed when a gas (usually argon) is introduced into a high current flowing between two or three electrodes. Ionization of the gas produces an inverted Y-shaped plasma. Unfortunately, early DCP instrumentation was prone to interference effects and also had some usability and reliability problems. For these reasons, the technique never became widely accepted by the analytical community (1). However, its one major benefit was that it could aspirate high levels of dissolved or suspended solids, because there was no restrictive sample injector for the solid material to block. This feature alone made it attractive for some laboratories, and once the initial limitations of DCPs



**Figure 1.** Schematic of an ICP-MS system showing the location of the plasma torch and radio frequency (RF) power supply.

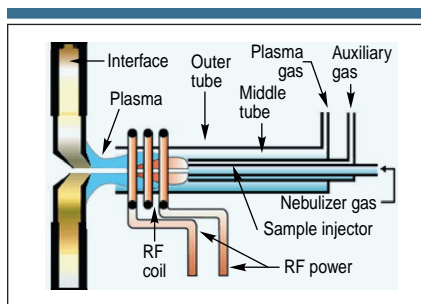
were better understood, the technique became more accepted. In fact, for those who want a DCP excitation source coupled with an optical emission instrument today, an Echelle-based grating using a solid-state detector is commercially available (2).

Limitations in the DCP approach led to the development of electrodeless plasma, of which the MIP was the simplest form. In this system, microwave energy (typically 100–200 W) is supplied to the plasma gas from an excitation cavity around a glass or quartz tube. The plasma discharge in the form of a ring is generated inside the tube. Unfortunately, even though the discharge achieves a very high power density, the high excitation temperatures exist only along a central filament. The bulk of the MIP never gets hotter than 2000–3000 K, which means it is prone to very severe matrix effects. In addition, they are easily extinguished dur-

ing aspiration of liquid samples. For these reasons, they have had limited success as an emission source, because they are not considered robust enough for the analysis of real-world, solution-based samples. However, they have gained acceptance as an ion source for mass spectrometry (3) and also as emission-based detectors for gas chromatography.

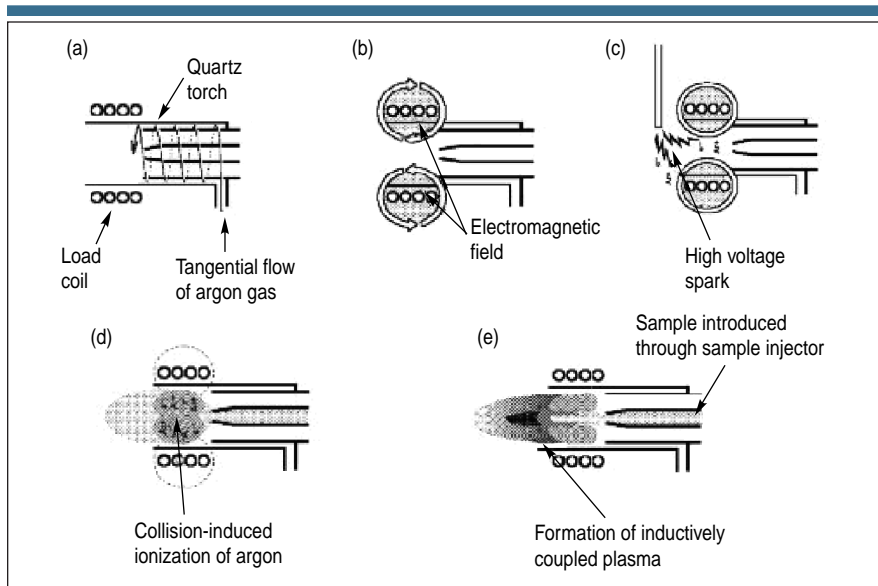
Because of the limitations of the DCP and MIP approaches, ICPs became the dominant focus of research for both optical emission and mass spectrometric studies. As early as 1964, Greenfield and co-workers reported that an atmospheric-pressure ICP coupled with OES could be used for elemental analysis (4). Although crude by today's standards, the system showed the enormous possibilities of the ICP as an excitation source and most definitely opened the door in the early 1980s to the even more exciting potential of using the ICP to generate ions (5).





**Figure 2.** Detailed view of a plasma torch and RF coil relative to the ICP-MS interface.

**Figure 3.** (right) Schematic of an ICP torch and load coil showing how the inductively coupled plasma is formed. (a) A tangential flow of argon gas is passed between the outer and middle tube of the quartz torch. (b) RF power is applied to the load coil, producing an intense electromagnetic field. (c) A high-voltage spark produces free electrons. (d) Free electrons are accelerated by the RF field, causing collisions and ionization of the argon gas. (e) The ICP is formed at the open end of the quartz torch. The sample is introduced into the plasma via the sample injector.



### THE PLASMA TORCH

Before we take a look at the fundamental principles behind the creation of an inductively coupled plasma used in ICP-MS, let us take a look at the basic compo-

nents that are used to generate the source: a plasma torch, a radio frequency (RF) coil, and RF power supply. Figure 1 shows their proximity to the rest of the instrument; Figure 2 is a more detailed view of the plasma torch and RF coil relative to the MS interface.

The plasma torch consists of three concentric tubes, which are usually made from quartz. In Figure 2, these are shown as the outer tube, middle tube, and sample injector. The torch can either be one-piece with all three tubes connected, or it can be a demountable design in which the tubes and the sample injector are separate. The gas (usually argon) used to form the plasma (plasma gas) is passed between the outer and middle tubes at a flow rate of  $\sim 12\text{--}17$  L/min. A second gas flow, the auxiliary gas, passes between the middle tube and the sample injector at  $\sim 1$  L/min and is used to change the position of the base of the plasma relative to the tube and the injector. A third gas flow, the nebulizer gas, also flowing at  $\sim 1$  L/min carries the sample, in the form of a fine-droplet aerosol, from the sample introduction system (for details, see Part II of this series: *Spectroscopy* **16**[5], 56–60 [2001]) and physically punches a channel through the center of the plasma. The sample injector is often made from materials other than quartz, such as alumina, platinum, and sapphire, if highly corrosive materials need to be analyzed. It is worth mentioning that although argon is the most suitable gas to use for all three flows, there are analytical benefits in using other gas mixtures, especially in the nebulizer flow (6). The plasma torch

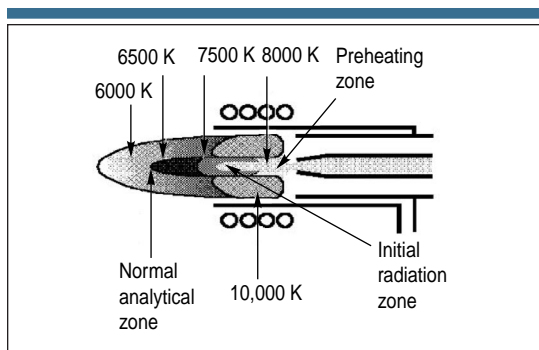


Figure 4. Different temperature zones in the plasma.

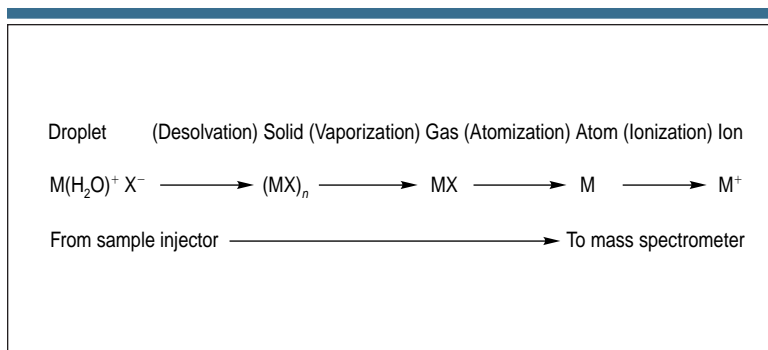


Figure 5. Mechanism of conversion of a droplet to a positive ion in the ICP.

is mounted horizontally and positioned centrally in the RF coil, approximately 10–20 mm from the interface. It must be emphasized that the coil used in an ICP-MS plasma is slightly different from the one used in ICP-OES. In all plasmas, there is a potential difference of a few hundred volts produced by capacitive coupling between the RF coil and the plasma. In an ICP mass spectrometer, this would result in a secondary discharge between the plasma and the interface cone, which could negatively affect the performance of the instrument. To compensate for this, the coil must be grounded to keep the interface region as close to zero potential as possible. I will discuss the full implications of this in greater detail in Part IV of this series.

#### FORMATION OF AN ICP DISCHARGE

Let us now discuss the mechanism of formation of the plasma discharge. First, a tangential (spiral) flow of argon gas is directed between the outer and middle tube of a quartz torch. A load coil, usually copper, surrounds the top end of the torch and is connected to a radio frequency generator. When RF power (typically 750–1500 W, depending on the sample) is applied to the load coil, an alternating current oscillates within the coil at a rate corresponding to the frequency of the generator. In most ICP generators this frequency is either 27 or 40 MHz. This RF oscillation of the current in the coil causes an intense electromagnetic field to be created in the area at the top of the torch. With argon gas flowing through the torch, a high-voltage spark is applied to the gas, which causes some electrons to be stripped from their argon atoms. These electrons, which are caught up and accelerated in the magnetic field, then collide with other argon atoms, stripping off still more electrons. This collision-

induced ionization of the argon continues in a chain reaction, breaking down the gas into argon atoms, argon ions, and electrons, forming what is known as an inductively coupled plasma discharge. The ICP discharge is then sustained within the torch and load coil as RF energy is continually transferred to it through the inductive coupling process. The sample aerosol is then introduced into the plasma through a third tube called the sample injector. This whole process is conceptually shown in Figure 3.

#### THE FUNCTION OF THE RF GENERATOR

Although the principles of an RF power supply have not changed since the work of Greenfield (4), the components have become significantly smaller. Some of the early generators that used nitrogen or air required 5–10 kW of power to sustain the plasma discharge — and literally took up half the room. Most of today's generators use solid-state electronic components, which means that vacuum power amplifier tubes are no longer required. This makes modern instruments significantly smaller and, because vacuum tubes were notoriously unreliable and unstable, far more suitable for routine operation.

As mentioned previously, two frequencies have typically been used for ICP RF generators: 27 and 40 MHz. These frequencies have been set aside specifically for RF applications of this kind, so they will not interfere with other communication-based frequencies. The early RF generators used 27 MHz, while the more recent designs favor 40 MHz. There appears to be no significant analytical advantage of one type over the other. However, it is worth mentioning that the 40-MHz design typically runs at lower power levels, which produces lower signal intensity and reduced background levels. Be-

cause it uses slightly lower power, this might be considered advantageous when it comes to long-term use of the generator.

The more important consideration is the coupling efficiency of the RF generator to the coil. The majority of modern solid-state RF generators are on the order of 70–75% efficient, meaning that 70–75% of the delivered power actually makes it into the plasma. This wasn't always the case, and some of the older vacuum tube-designed generators were notoriously inefficient; some of them experienced more than a 50% power loss. Another important criterion to consider is the way the matching network compensates for changes in impedance (a material's resistance to the flow of an electric current) produced by the sample's matrix components or differences in solvent volatility. In older crystal-controlled generators, this was usually done with servo-driven capacitors. They worked very well with most sample types, but because they were mechanical devices, they struggled to compensate for very rapid impedance changes produced by some samples. As a result, the plasma was easily extinguished, particularly during aspiration of volatile organic solvents.

These problems were partially overcome by the use of free-running RF generators, in which the matching network was based on electronic tuning of small changes in frequency brought about by the sample solvent or matrix components. The major benefit of this approach was that compensation for impedance changes was virtually instantaneous because there were no moving parts. This allowed for the successful analysis of many sample types that would probably have extinguished the plasma of a crystal-controlled generator.

### IONIZATION OF THE SAMPLE

To better understand what happens to the sample on its journey through the plasma source, it is important to understand the different heating zones within the discharge. Figure 4 shows a cross-sectional representation of the discharge along with the approximate temperatures for different regions of the plasma.

As mentioned previously, the sample aerosol enters the injector via the spray chamber. When it exits the sample injector, it is moving at such a velocity that it physically punches a hole through the center of the plasma discharge. It then goes through a number of physical changes, starting at the preheating zone and continuing through the radiation

zone before it eventually becomes a positively charged ion in the analytical zone. To explain this in a very simplistic way, let's assume that the element exists as a trace metal salt in solution. The first step that takes place is desolvation of the droplet. With the water molecules stripped away, it then becomes a very small solid particle. As the sample moves further into the plasma, the solid particle changes first into a gaseous form and then into a ground-state atom. The final process of conversion of an atom to an ion is achieved mainly by collisions of energetic argon electrons (and to a lesser extent by argon ions) with the ground-state atom (7). The ion then emerges from the plasma and is directed into the interface of the mass spectrometer (for details on the mechanisms of ion generation, please refer to Part I of this series: *Spectroscopy* **16**[4], 38–42 [2001]). This process of conversion of droplets into ions is represented in Figure 5.

The next installment of this series will focus on probably the most crucial area of an ICP mass spectrometer — the interface region — where the ions generated in the atmospheric plasma have to be sampled with consistency and electrical integrity by the mass spectrometer, which is under extremely high vacuum.

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