A Beginner's Guide to ICP-MS

Part II: The Sample-Introduction System

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Part II of Robert Thomas' series on inductively coupled plasma mass spectrometry looks at one of the most critical areas of the instrument — the sample introduction system. He discusses the fundamental principles of converting a liquid into a fine-droplet aerosol suitable for ionization in the plasma, and provides an overview of the different types of commercially available nebulizers and spray chambers.

The majority of inductively coupled plasma mass spectrometry (ICP-MS) applications involve the analysis of liquid samples. Even though spectroscopists adapted the technique over the years to handle solids, it was developed in the early 1980s primarily to analyze solutions. There are many ways of introducing a liquid into an ICP mass spectrometer, but they all basically achieve the same result — they generate a fine aerosol of the sample so it can be efficiently ionized in the plasma discharge. The sample-introduction area has been called the Achilles heel of ICP-MS because it is considered the weakest component of the instrument, with only 1–2% of the sample finding its way into the plasma (1). Although there has recently been much improvement in this area, the fundamental design of an ICP-MS sample introduction system has not dramatically changed since the technique was first introduced in 1983.

Before discussing the mechanics of aerosol generation in greater detail, let us look at the basic components of a sample introduction system. Figure 1 shows the proximity of the sample introduction area relative to the rest of the ICP mass spectrometer, while Figure 2 represents the individual components.

The mechanism of introducing a liquid sample into analytical plasma can be considered as two separate events — aerosol generation using a nebulizer and droplet selection by way of a spray chamber. Sharp carried out a thorough investigation of both processes (2).

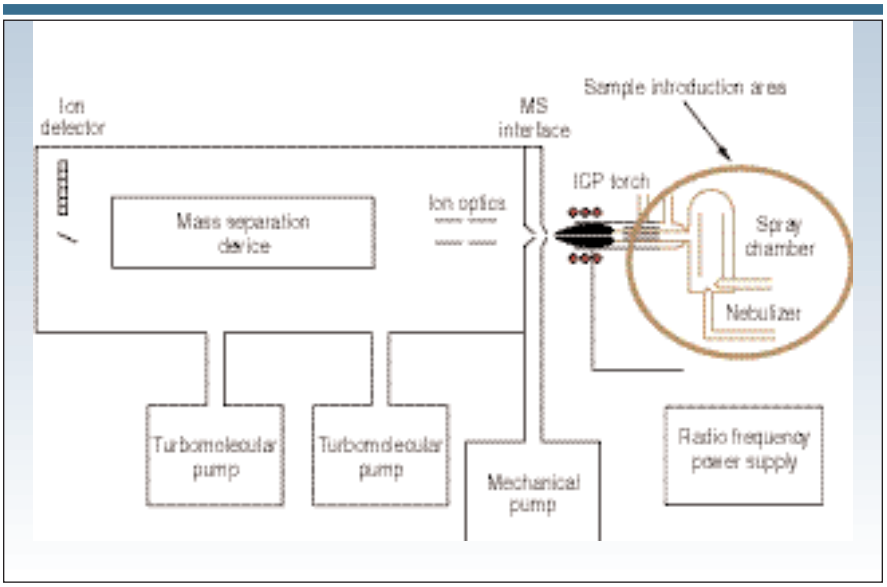

Figure 1. ICP-MS system diagram showing the location of the sample introduction area.

AEROSOL GENERATION

As mentioned previously, the main function of the sample introduction system is to generate a fine aerosol of the sample. It achieves this purpose with a nebulizer and a spray chamber. The sample is normally pumped at ~1 mL/min via a peristaltic pump into the nebulizer. A peristaltic pump is a small pump with lots of minirollers that rotate at the same speed. The constant motion and pressure of the rollers on the pump tubing feed the sample to the nebulizer. The benefit of a peristaltic pump is that it ensures a constant flow of liquid, irrespective of differences in viscosity between samples, standards, and blanks. After the sample enters the nebulizer, the liquid is broken up into a fine aerosol by the pneumatic action of gas flow (~1 L/min) smashing the liquid into tiny droplets, which is very similar to the spray mechanism of a can of deodorant. Although pumping the sample is the most common approach to introducing it, some pneumatic nebulizers, such as the concentric design, don't need a pump because they rely on the natural venturi effect of the positive pressure of the nebulizer gas to suck the sample through the tubing. Solution nebulization is conceptually represented in Figure 3, which shows aerosol generation using a nebulizer with a crossflow design.

DROPLET SELECTION

Because the plasma discharge is inefficient at dissociating large droplets, the spray chamber's function is primarily to allow only the small droplets to enter the plasma. Its secondary purpose is to smooth out pulses that occur during the nebulization process, due mainly to the peristaltic pump. Several ways exist to en-

sure only the small droplets get through, but the most common way is to use a double-pass spray chamber where the aerosol emerges from the nebulizer and is directed into a central tube running the whole length of the chamber. The droplets travel the length of this tube, where the large droplets (greater than ~10 µm in diameter) fall out by gravity and exit through the drain tube at the end of the spray chamber. The fine droplets (~5–10 µm in diameter) then pass between the outer wall and the central tube, where they eventually emerge from the spray chamber and are transported into the sample injector of the plasma torch (3). Although many different designs are available, the spray chamber's main function is to allow only the smallest droplets into the plasma for dissociation, atomization, and finally ionization of the sample's elemental components. Figure 4 presents a simplified schematic of this process.

Let us now look at the different nebulizer and spray chamber designs that are most commonly used in ICP-MS. This article cannot cover every type available because a huge market has developed over the past few years for application-specific customized sample introduction components. This market created an industry of small OEM (original equipment manufacturers) companies that manufacture parts for instrument companies as well as selling directly to ICP-MS users.

NEBULIZERS

By far the most common design used for ICP-MS is the pneumatic nebulizer, which uses mechanical forces of a gas flow (normally argon at a pressure of 20–30 psi) to generate the sample aerosol. The most popular designs of pneumatic nebulizers include concentric, microconcentric, microflow, and crossflow. They are usually made from glass, but other nebulizer materials, such as various kinds of polymers, are becoming more popular, particularly for highly corrosive samples and specialized applications. I want to emphasize at this point that nebulizers designed for use with ICP-optical emission spectroscopy (OES) are not recommended for ICP-MS. This fact results from a limitation in total dissolved solids (TDS) that can be put into the ICP-MS interface area. Because the orifice sizes of the sampler and skimmer cones used in ICP-MS are so small (~0.6–1.2 mm), the concentration of matrix components must generally be kept below 0.2%

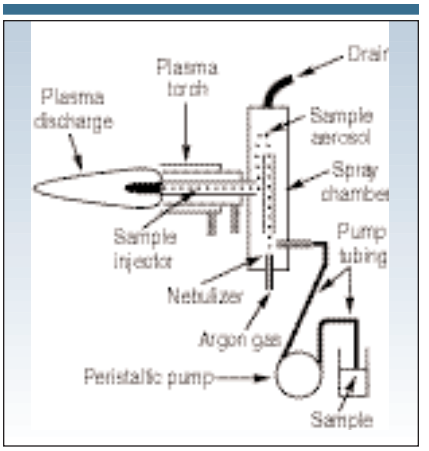

Figure 2. Diagram of the ICP-MS sample introduction area.

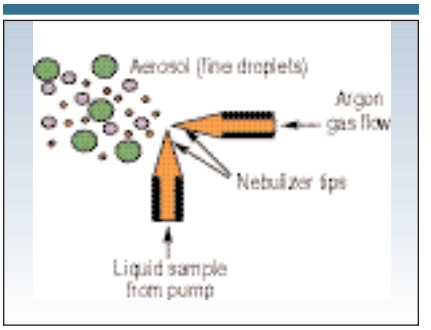

Figure 3. Conceptual representation of aerosol generation with an ICP-MS nebulizer.

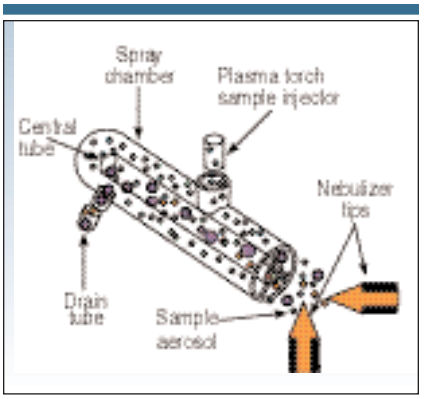

Figure 4. Simplified representation of the separation of large and fine droplets in the spray chamber.

(4). Therefore, general-purpose ICP-OES nebulizers that are designed to aspirate 1–2% dissolved solids, or high-solids nebulizers such as the Babbington, V-groove, or cone-spray nebulizers, which are designed to handle as much as 20% dissolved solids, are not ideal for use with ICP-MS. The most common of the pneumatic nebulizers used in commercial ICP mass spectrometers are the concentric and crossflow designs. The concentric design is more suitable for clean samples, while the crossflow is generally more tolerant to samples containing higher levels of solids or particulate matter.

Concentric design. In the concentric nebulizer, the solution is introduced through a capillary tube to a low-pressure region created by a gas flowing rapidly past the end of the capillary. The low pressure and high-speed gas combine to break up the solution into an aerosol, which forms at the open end of the nebulizer tip. Figure 5 illustrates the concentric design.

Concentric pneumatic nebulizers can provide excellent sensitivity and stability, particularly with clean solutions. However, the small orifices can be plagued by blockage problems, especially if large numbers of heavy matrix samples are aspirated.

Crossflow design. For samples that contain a heavier matrix or small amounts of undissolved matter, the crossflow design is probably the best option. With this design the argon gas is directed at right angles to the tip of a capillary tube, in contrast to the concentric design, where the gas flow is parallel to the capillary. The solution is either drawn up through the capillary tube via the pressure created by the high-speed gas flow or, as is most common with crossflow nebulizers, forced through the tube with a peristaltic pump. In either case, contact between the high-speed gas and the liquid stream causes the liquid to break up into an aerosol. Crossflow nebulizers are generally not as efficient as concentric nebulizers at creating the very small droplets needed for ICP-MS analyses. However, the larger diameter liquid capillary and longer distance between liquid and gas injectors reduce clogging problems. Many analysts feel that the small penalty paid in analytical sensitivity and precision when compared with concentric nebulizers is compensated by the fact that the crossflow design is far more rugged for routine use. Figure 6 shows a cross section of a crossflow nebulizer.

Microflow design. A new breed of nebulizers is being developed for ICP-MS called microflow nebulizers, which are designed to operate at much lower sample flows. While conventional nebulizers have a sample uptake rate of about 1 mL/min, microflow nebulizers typically run at less than 0.1 mL/min. They are based on the concentric principle, but

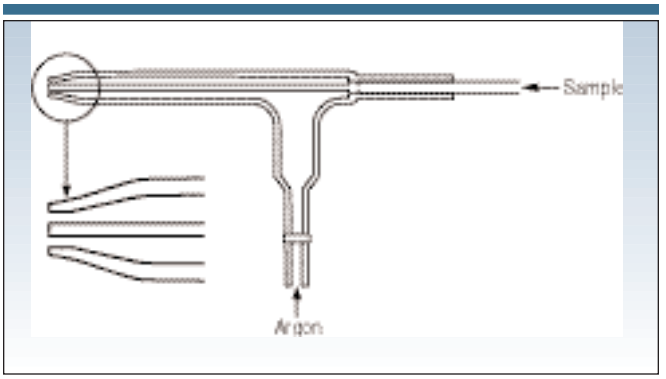

Figure 5. Diagram of a typical concentric nebulizer.

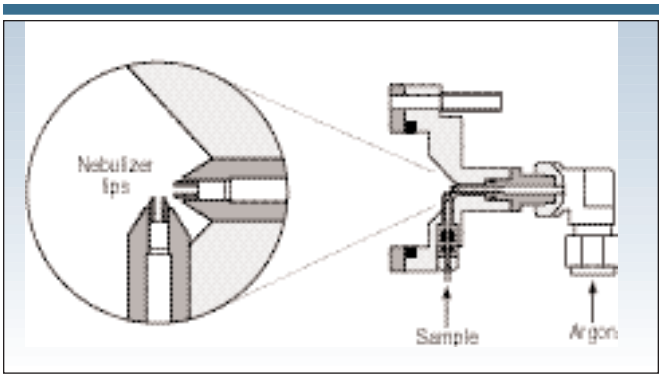

Figure 6. Schematic of a crossflow nebulizer.

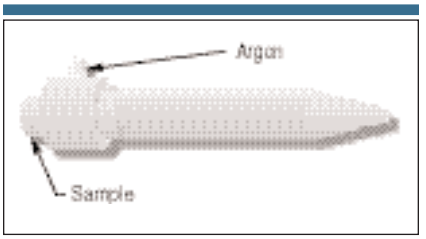

Figure 7. A typical concentric microflow nebulizer. Printed with permission from Elemental Scientific (Omaha, NE).

they usually operate at higher gas pressure to accommodate the lower sample flow rates. The extremely low uptake rate makes them ideal for applications with limited sample volume or where the sample or analyte is prone to sample introduction memory effects. These nebulizers and their components are typically constructed from polymer materials such as polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA), or polyvinylidene fluoride (PVDF). In fact, their excellent corrosion resistance means that they have naturally low blank levels. This characteristic, together with their ability to handle small sample volumes such as vapor-phase decomposition (VPD) applications, makes them an ideal choice for semiconductor labs that are carrying out ultra-trace element analysis (5). A typical microflow nebulizer made from PFA is shown in Figure 7.

SPRAY CHAMBERS

Let us now turn our attention to spray chambers. Basically two designs are used in commercial ICP-MS instrumentation — double pass and cyclonic spray chambers. The double pass is by far the most common, with the cyclonic type gaining in popularity. Another type of spray chamber based on the impact bead design (first developed for flame AA and then adapted for ICP-OES) was tried on the early ICP-MS systems with limited success, but is not generally used today. As mentioned earlier, the function of the spray chamber is to reject the larger aerosol droplets and also to smooth out pulses produced by the peristaltic pump. In addition, some ICP-MS spray chambers are externally cooled (typically to 2–5 °C) for thermal stability of the sample and to minimize the amount of solvent going into the plasma. This can have a number of beneficial effects, depending on the application, but the main benefits are reduction of oxide species and the ability to aspirate volatile organic solvents.

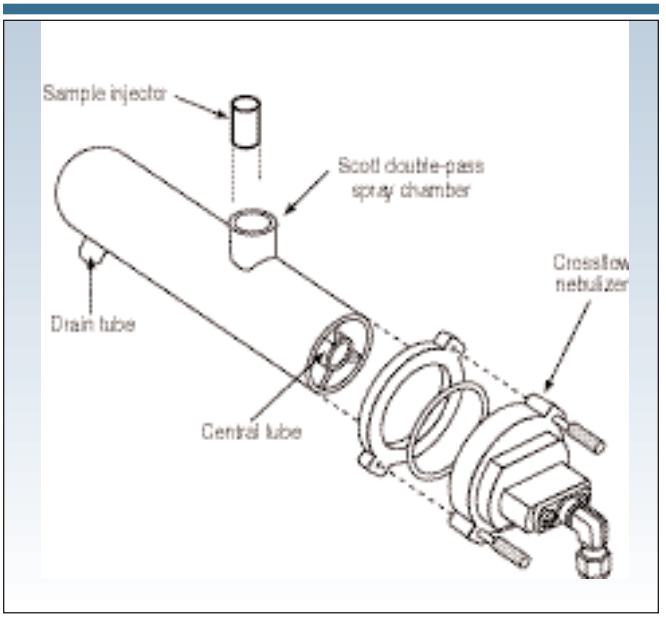

Figure 8. Schematic of a Scott double-pass spray chamber (shown with crossflow nebulizer). Printed with permission of PerkinElmer Instruments (Norwalk, CT).

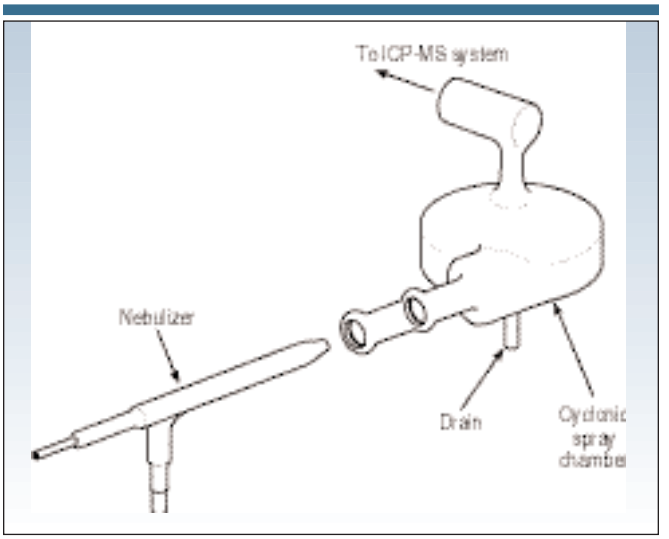

Figure 9. Schematic of a cyclonic spray chamber (shown with concentric nebulizer).

Double pass. By far the most common design of double-pass spray chamber is the Scott design, which selects the small droplets by directing the aerosol into a central tube. The larger droplets emerge from the tube and, by gravity, exit the spray chamber via a drain tube. The liquid in the drain tube is kept at positive pressure (usually by way of a loop), which forces the small droplets back between the outer wall and the central tube, where they emerge from the spray chamber into the sample injector of the plasma torch. Scott double-pass spray chambers come in a variety of shapes, sizes, and materials, but are generally considered the most rugged design for routine use. Figure 8 shows a Scott spray chamber made of a polysulfide-type material, coupled to a crossflow nebulizer.

Cyclonic spray chamber. The cyclonic spray chamber operates by centrifugal force. Droplets are discriminated according to their size by means of a vortex produced by the tangential flow of the sample aerosol and argon gas inside the chamber. Smaller droplets are carried with the gas stream into the ICP-MS, while the larger droplets impinge on the walls and fall out through the drain. It is generally accepted that a cyclonic spray chamber has a higher sampling efficiency, which, for clean samples, translates into higher sensitivity and lower detection limits. However, the droplet size distribution appears to be different from a double-pass design, and for certain types of samples, can give slightly inferior precision. An excellent evaluation of the capabilities of a cyclonic spray chamber was made by Beres and co-workers (6). Figure 9 shows a cyclonic spray chamber connected to a concentric nebulizer.

Many other nonstandard sample introduction devices are available that are not described in this particular tutorial, such as ultrasonic nebulization, membrane desolvation, flow injection, direct injection, electrothermal vaporization, and laser ablation. However, they are becoming more and more important, particularly as ICP-MS users are demanding higher performance and more flexibility. For that reason, they will be addressed in a separate tutorial at the end of this series.

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