A Beginner's Guide to ICP-MS

Part I

ROBERT THOMAS

Amazingly, 18 years after the commercialization of inductively coupled plasma mass spectrometry (ICP-MS), less than 4000 systems have been installed worldwide. If you compare this number with another rapid multielement technique, inductively coupled plasma optical emission spectrometry (ICP-OES), first commercialized in 1974, the difference is quite significant. In 1992, 18 years after ICP-OES was introduced, more than 9000 units had been sold, and if you compare it with the same time period that ICP-MS has been available, the difference is even more dramatic. From 1983 to the present day, more than 17,000 ICP-OES systems have been installed — more than four times the number of ICP-MS systems. If the comparison is made with all atomic spectroscopy instrumentation (ICP-MS, ICP-OES, graphite furnace atomic absorption [GFAA] and flame atomic absorption [FAA]), the annual turnover for ICP-MS is less than 7% of the total atomic spectroscopy market — 400 units compared to approximately 6000 atomic spectroscopy systems. It's even more surprising when you consider that ICP-MS offers so much more than the other techniques, including two of its most attractive features — the rapid multielement capabilities of ICP-OES, combined with the superb detection limits of GFAA.

ICP-MS — ROUTINE OR RESEARCH?

Clearly, one of the reasons is price — an ICP-MS system typically costs twice as much as an ICP-OES system and three times more than a GFAA system. But in a competitive world, the "street price" of an ICP-MS system is much closer to a top-of-the-line ICP-OES system fitted with sampling accessories or a GFAA system that has all the bells and whistles on it. So if ICP-MS is not significantly more expensive than ICP-OES and GFAA, why hasn't it been more widely accepted by the analytical community? I firmly believe that the major reason why ICP-MS has not gained the popularity of the other trace element techniques is that it is still considered a complicated research technique, requiring a very skilled person to operate it. Manufacturers of ICP-MS equipment are constantly striving to make the systems easier to operate, the software easier to use, and the hardware easier to maintain, but even after 18 years it is still not perceived as a mature, routine tool like flame AA or ICP-OES. This might be partially true because of the relative complexity of the instrumentation; however, in my opinion, the dominant reason for this misconception is that there has not been good literature available explaining the basic principles and benefits of ICP-MS in a way that is compelling and easy to understand for someone with very little knowledge of the technique. Some excellent textbooks (1, 2) and numerous journal papers (3–5) are available that describe the fundamentals, but they tend to be far too heavy for a novice reader. There is no question in my mind that the technique needs to be presented in a more user-friendly way to make routine analytical laboratories more comfortable with it. Unfortunately, the publishers of the "for Dummies" series of books have not yet found a mass (excuse the pun) market for writing one on ICP-MS. So until that time, we will be presenting a number of short tutorials on the technique, as a follow-up to the poster that was included in the February 2001 issue of *Spectroscopy*.

During the next few months, we will be discussing the following topics in greater depth:

- principles of ion formation
- sample introduction
- plasma torch/radio frequency generator
- interface region
- ion focusing
- mass separation
- ion detection
- sampling accessories
- applications.

We hope that by the end of this series, we will have demystified ICP-MS, made it

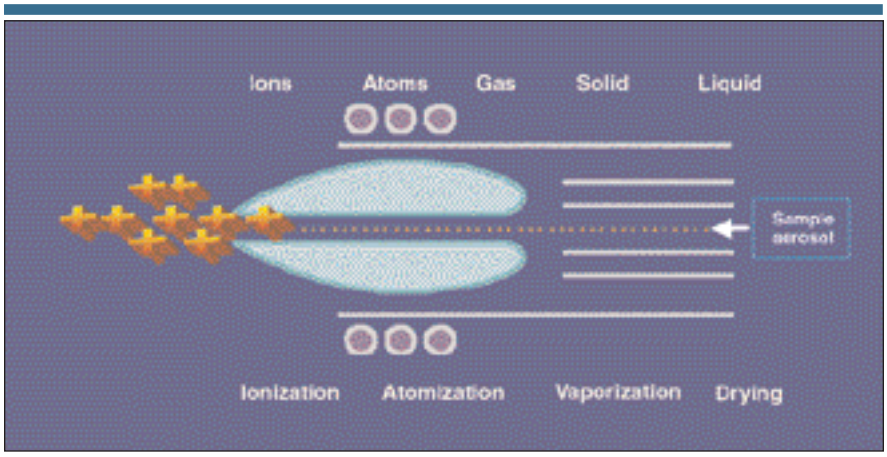

Figure 1. Generation of positively charged ions in the plasma.

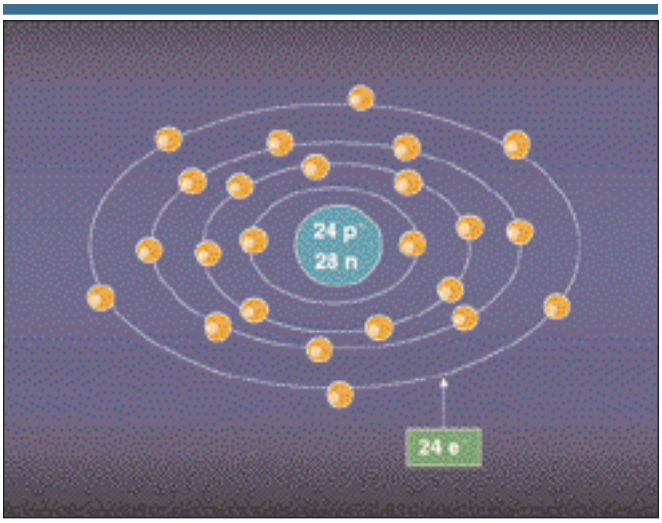

Figure 2. Simplified schematic of a chromium ground-state atom (Cr^0).

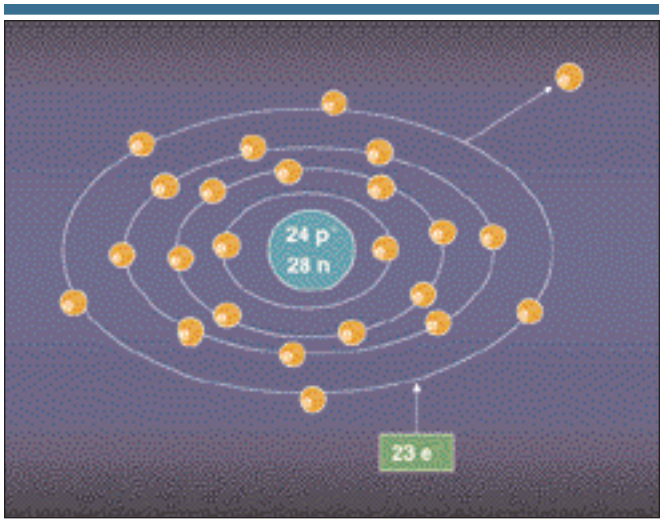

Figure 3. Conversion of a chromium ground-state atom (Cr^0) to an ion (Cr^+).

a little more compelling to purchase, and ultimately opened up its potential as a routine tool to the vast majority of the trace element community that has not yet realized the full benefits of its capabilities.

GENERATION OF IONS IN THE PLASMA

We'll start this series off with a brief description of the fundamental principle used in ICP-MS — the use of a high-temperature plasma discharge to generate positively charged ions. The sample, typically in liquid form, is pumped into the sample introduction system, which is made up of a spray chamber and nebulizer. It emerges as an aerosol and eventually finds its way — by way of a sample injector — into the base of the plasma. As it travels through the different heating zones of the plasma torch it is dried, vaporized, atomized, and ionized. During this time, the sample is transformed from a liquid aerosol to solid particles, then into a gas. When it finally arrives at the analytical zone of the plasma, at approximately 6000–7000 K, it exists as excited atoms and ions, representing the elemental composition of the sample.

The excitation of the outer electron of a ground-state atom, to produce wavelength-specific photons of light, is the fundamental basis of atomic emission. However, there is also enough energy in the plasma to remove an electron from its orbital to generate an ion. It is the generation, transportation, and detection of significant numbers of these positively charged ions that give ICP-MS its characteristic ultratrace detection capabilities.

It is also important to mention that, although ICP-MS is predominantly used for the detection of positive ions, negative ions (such as halogens) are also produced in the plasma. However, because the extraction and transportation of negative ions is different from that of positive ions, most commercial instruments are not designed to measure them. The process of the generation of positively charged ions in the plasma is shown conceptually in greater detail in Figure 1.

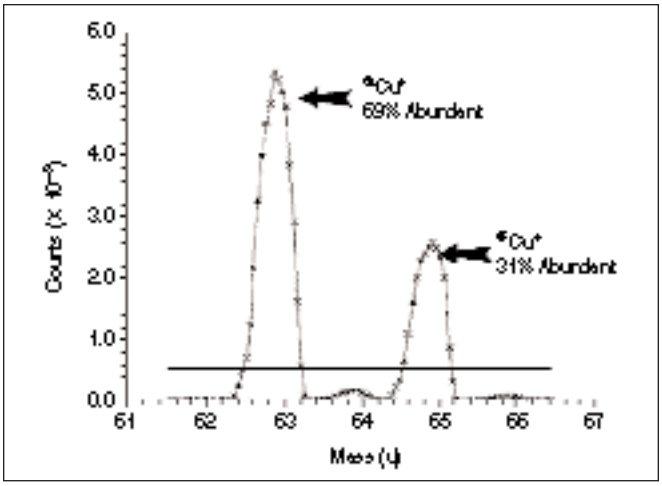

Figure 4. Mass spectra of the two copper isotopes — $^{63}Cu^{+}$ and $^{65}Cu^{+}$.

Table I. Breakdown of the atomic structure of copper isotopes.

	^{63}Cu	^{65}Cu
Number of protons (p^+)	29	29
Number of electrons (e^-)	29	29
Number of neutrons (n)	34	36
Atomic mass ($p^+ + n$)	63	65
Atomic number (p^+)	29	29
Natural abundance	69.17%	30.83%
Nominal atomic weight	63.55*	

* Calculated using the formulae $0.6917n + 0.3083n + p^+$ (referenced to the atomic weight of carbon)

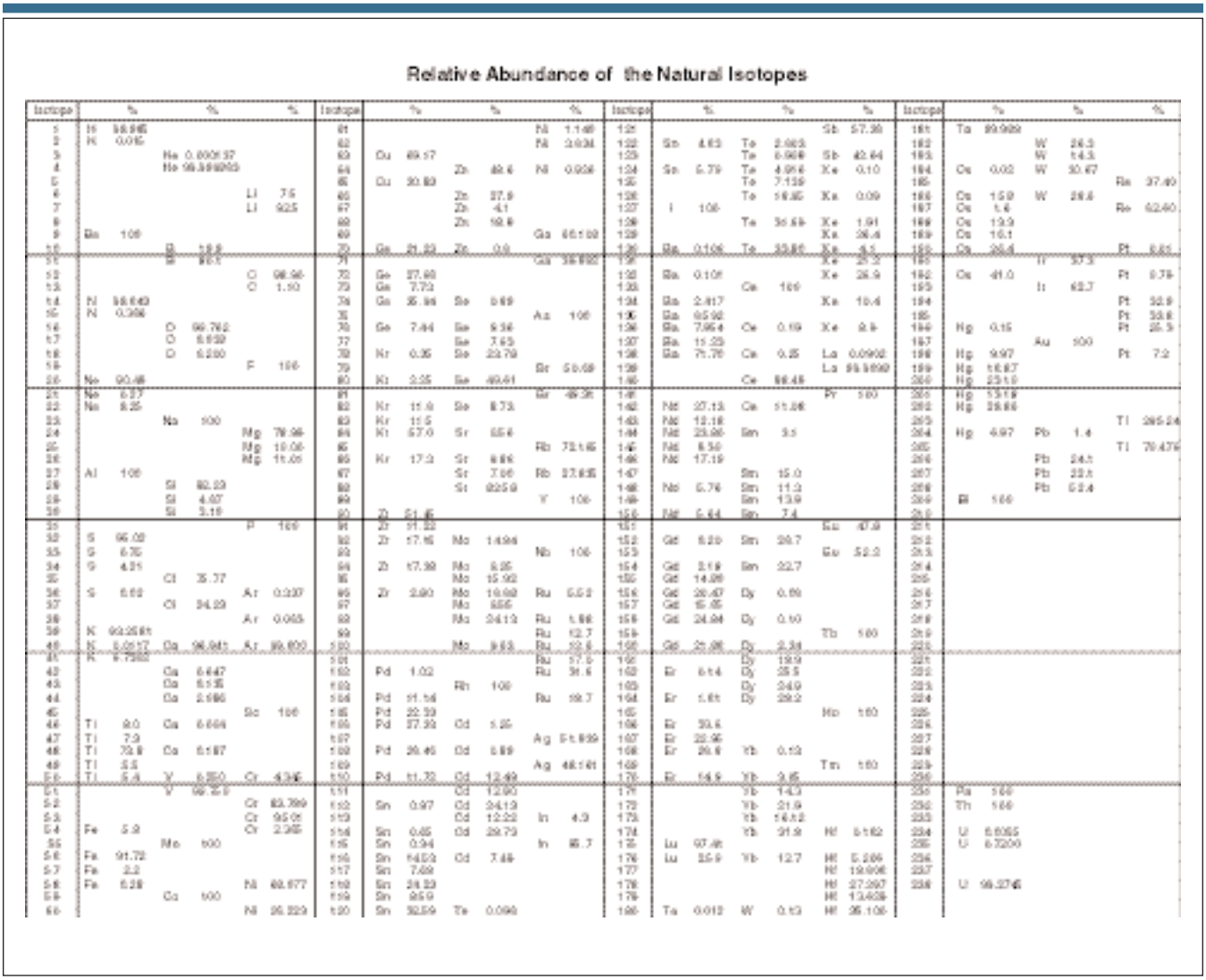

Figure 5. Relative abundance of the naturally occurring isotopes of all the elements (6). Reproduced with the permission of PerkinElmer Instruments (Norwalk, CT).

ION FORMATION

Figures 2 and 3 show the actual process of conversion of a neutral ground-state atom to a positively charged ion. Figure 2 shows a very simplistic view of the chromium atom Cr^0, consisting of a nucleus with 24 protons (p^+) and 28 neutrons (n), surrounded by 24 orbiting electrons (e^-) (It must be emphasized that this is not meant to be an accurate representation of the electrons' shells and subshells, but simply a conceptual explanation for the purpose of clarity). From this we can say that the atomic number of chromium is 24 (number of protons), and its atomic mass is 52 (number of protons + neutrons).

If energy is then applied to the chromium ground-state atom in the form of heat from a plasma discharge, one of the orbiting electrons will be stripped off the outer shell. This will result in only 23 electrons left orbiting the nucleus. Because the atom has lost a negative charge (e^-) but still has 24 protons (p^+) in the nucleus, it is converted into an ion with a net positive charge. It still has an atomic mass of 52 and an atomic number of 24, but is now a positively charged ion and not a neutral ground-state atom. This process is shown in Figure 3.

NATURAL ISOTOPES

This is a very basic look at the process, because most elements occur in more than one form (isotope). In fact, chromium has four naturally occurring isotopes, which means that the chromium atom exists in four different forms, all with the same atomic number of 24 (number of protons), but with different atomic masses (numbers of neutrons).

To make this a little easier to understand, let's take a closer look at an element like copper, which has only two different isotopes — one with an atomic mass of 63 (^{63}Cu) and the other with an atomic mass of 65 (^{65}Cu). They both have the same number of protons and electrons, but differ in the number of neutrons in the nucleus. The natural abundances of ^{63}Cu and ^{65}Cu are 69.1% and 30.9%, respectively, which gives copper a nominal atomic mass of 63.55 — the value you see for copper in atomic weight reference tables. Details of the atomic structure of the two copper isotopes are shown in Table I.

When a sample containing naturally occurring copper is introduced into the plasma, two different ions of copper, $^{63}Cu^+$ and $^{65}Cu^+$, are produced, which generate different mass spectra — one at mass 63 and another at mass 65. This can be seen in Figure 4, which is an actual ICP-MS spectral scan of a sample containing copper. It shows a peak for the $^{63}Cu^+$ ion on the left, which is 69.17% abundant, and a peak for $^{65}Cu^+$ at 30.83% abundance, on the right. You can also see small peaks for two Zn isotopes at mass 64 (^{64}Zn) and mass 66 (^{66}Zn) (Zn has a total of five isotopes at masses 64, 66, 67, 68, and 70). In fact, most elements have at least two or three isotopes and many elements, including zinc and lead, have four or more isotopes. Figure 5 is a chart that shows the relative abundance of the naturally occurring isotopes of all the elements.

During the next few months, we will systematically take you on a journey through the hardware of an ICP mass spectrometer, explaining how each major component works, and finishing the series with an overview of how the technique is being used to solve real-world application problems. Our goal is to present both the basic principles and benefits of the technique in a way that is clear, concise, and very easy to understand. We hope that by the end of the series, you and your managers will be in a better position to realize the enormous benefits that ICP-MS can bring to your laboratory.

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Robert Thomas *is the principal of his own freelance writing and scientific consulting company, Scientific Solutions, based in Gaithersburg, MD. He can be contacted by email at thomasrj@bellatlantic.net or via his web site at www.scientificsolutions1.com.*◆

A Beginner's Guide to ICP-MS

Part II: The Sample-Introduction System

ROBERT THOMAS

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).

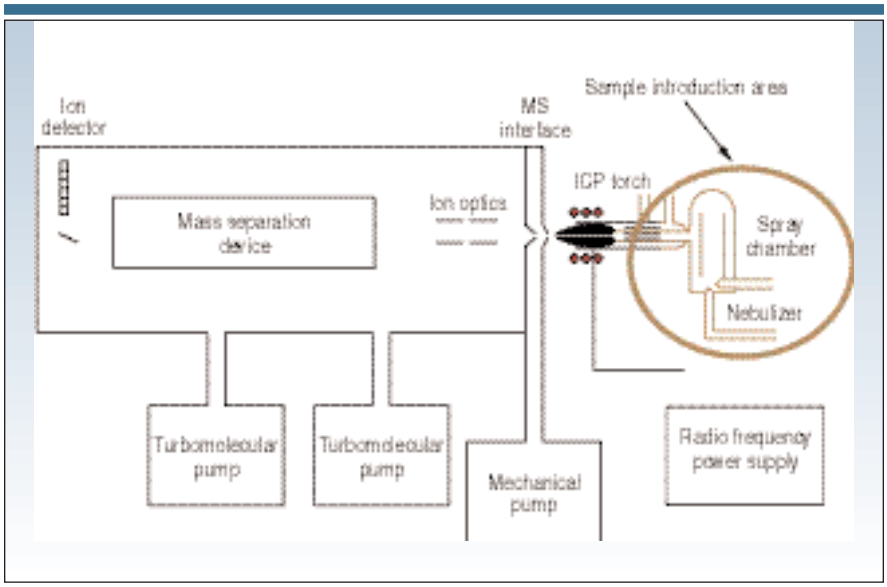

Figure 1. ICP-MS system diagram showing the location of the sample introduction area.

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%

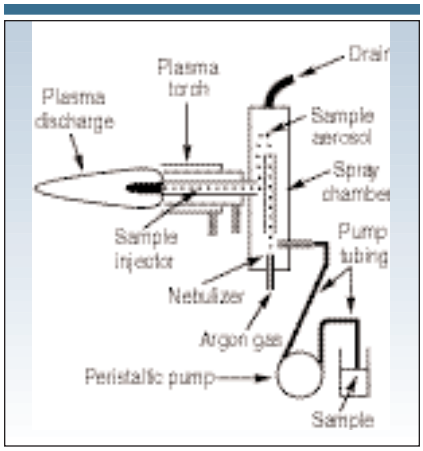

Figure 2. Diagram of the ICP-MS sample introduction area.

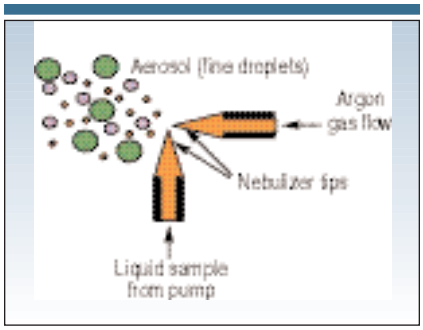

Figure 3. Conceptual representation of aerosol generation with an ICP-MS nebulizer.

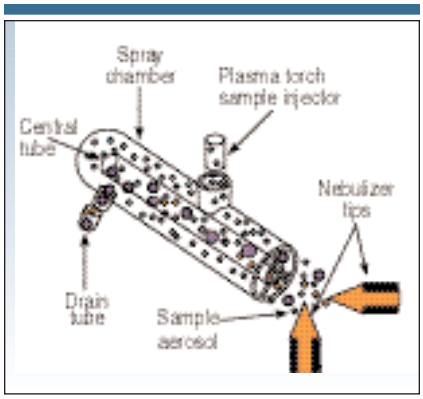

Figure 4. Simplified representation of the separation of large and fine droplets in the spray chamber.

(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

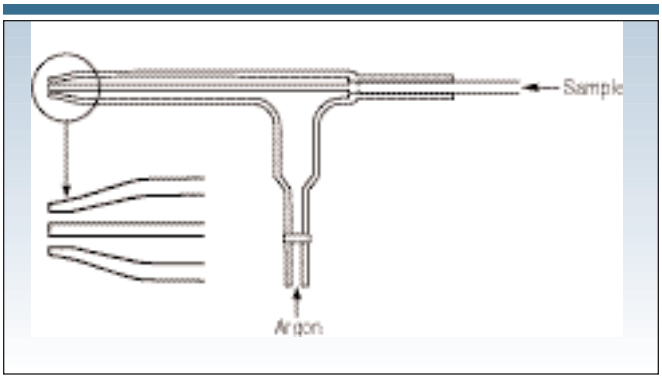

Figure 5. Diagram of a typical concentric nebulizer.

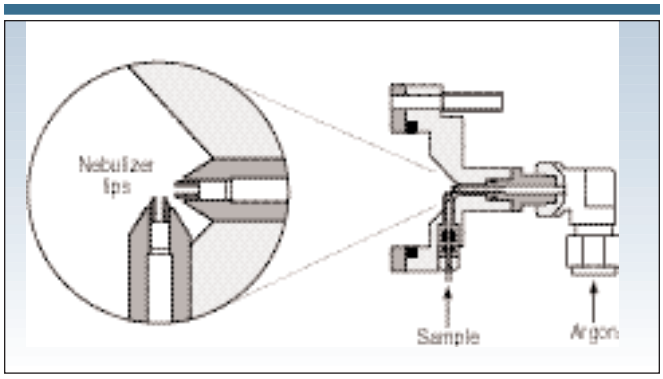

Figure 6. Schematic of a crossflow nebulizer.

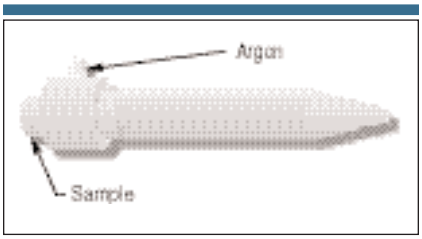

Figure 7. A typical concentric microflow nebulizer. Printed with permission from Elemental Scientific (Omaha, NE).

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.

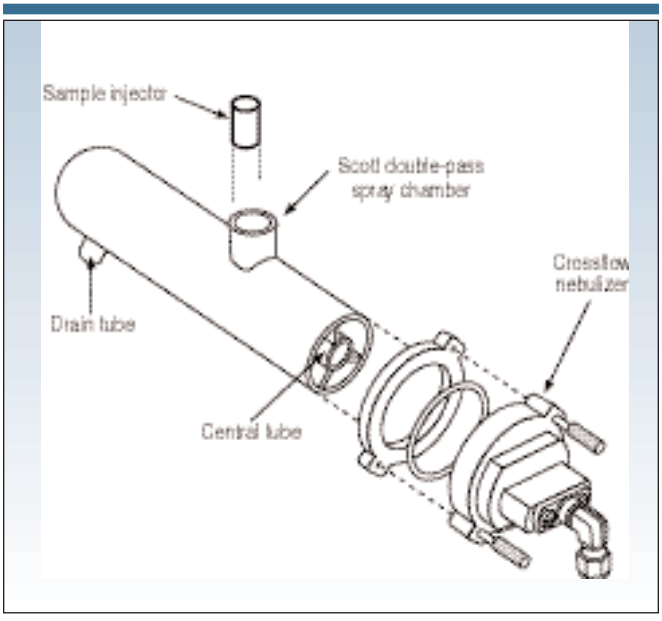

Figure 8. Schematic of a Scott double-pass spray chamber (shown with crossflow nebulizer). Printed with permission of PerkinElmer Instruments (Norwalk, CT).

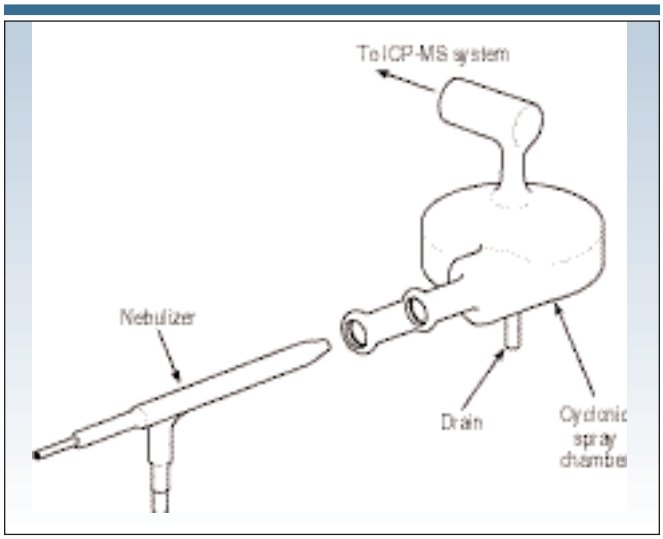

Figure 9. Schematic of a cyclonic spray chamber (shown with concentric nebulizer).

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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Robert Thomas *is the principal of his own freelance writing and scientific marketing consulting company, Scientific Solutions, based in Gaithersburg, MD. He specializes in trace element analysis and can be contacted by e-mail at thomasrj@bellatlantic.net or via his web site at www.scientificsolutions1.com.* ◆

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TRAINING COURSES

Thermo Nicolet (Madison, WI) is offering a free Spring 2001 Spectroscopic Solutions Seminar Series. The seminars will cover basic FT-IR spectroscopy, microspectroscopy, dispersive Raman microscopy, Raman spectroscopy, and specialized sampling techniques. This year's schedule includes the following seminars:

May 22 at the Syracuse Sheraton, Syracuse, NY; May 24 at the Wyndham Westborough Hotel, Westborough, MA; May 24 at the Marriott Oak Brook, Oak Brook, IL; June 5 at the East Lansing Marriott, East Lansing, MI; June 5 at the Embassy Suites, Overland Park, KS; June 7 at the Sheraton Indianapolis, Indianapolis, IN; June 12 at the Delta Meadowvale Conference Center, Mississauga, Ontario, Canada; June 12 at the Embassy Suites, Brookfield, WI; July 10 at the Coast Terrace Inn, Edmonton, Alberta, Canada; and July 26 at the Ala Moana Hotel, Honolulu, HI.

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A Beginner's Guide to ICP-MS

Part III: The Plasma Source

ROBERT THOMAS

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 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).

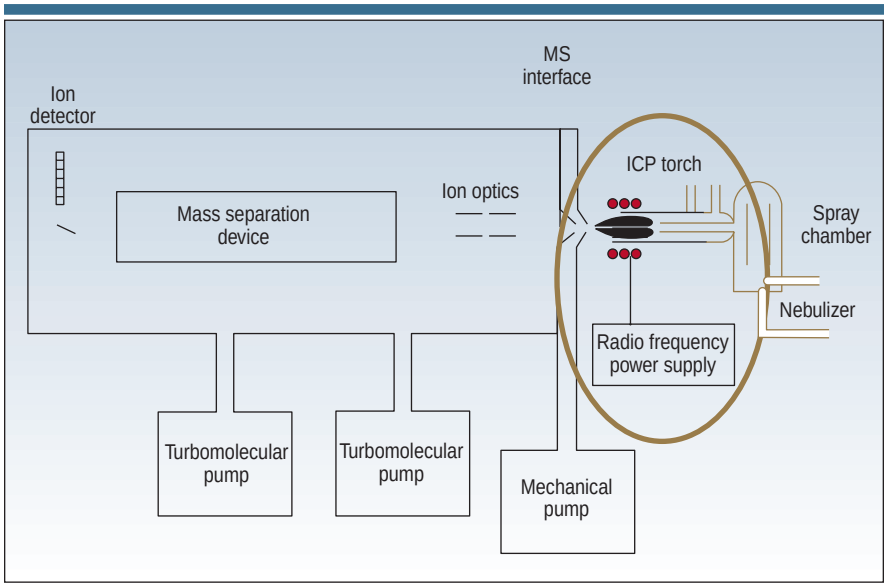

Figure 1. Schematic of an ICP-MS system showing the location of the plasma torch and radio frequency (RF) power supply.

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 during 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).

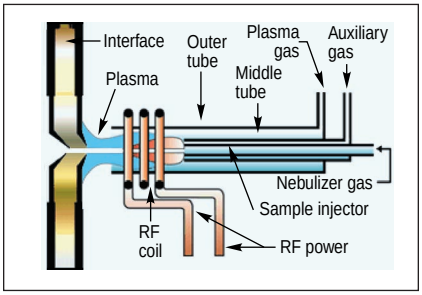

Figure 2. Detailed view of a plasma torch and RF coil relative to the ICP-MS interface.

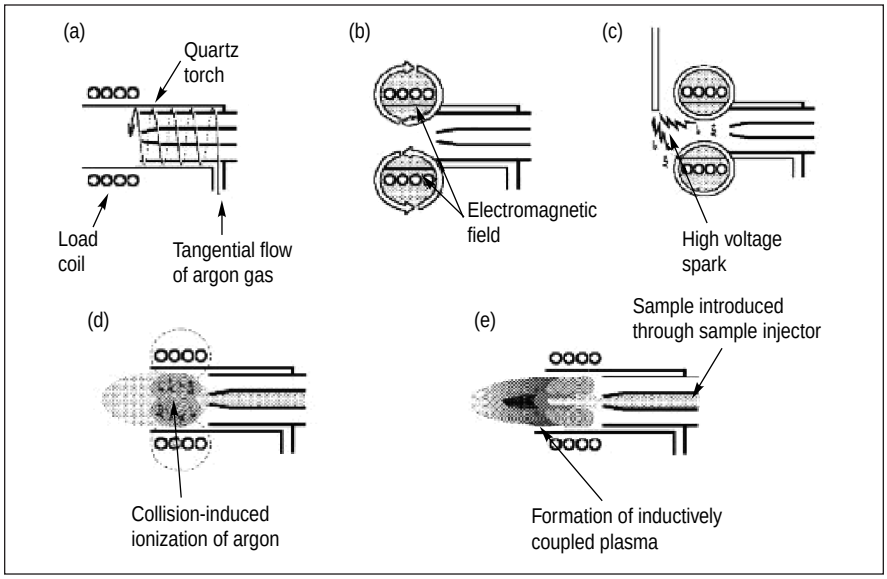

Figure 3. (right) Schematic of an ICP torch and load coil showing how the inductively coupled plasma is formed. (a) A tangential flow of argon gas is passed between the outer and middle tube of the quartz torch. (b) RF power is applied to the load coil, producing an intense electromagnetic field. (c) 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 components 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 ~12–17 L/min. A second gas flow, the auxiliary gas, passes between the middle tube and the sample injector at ~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 ~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

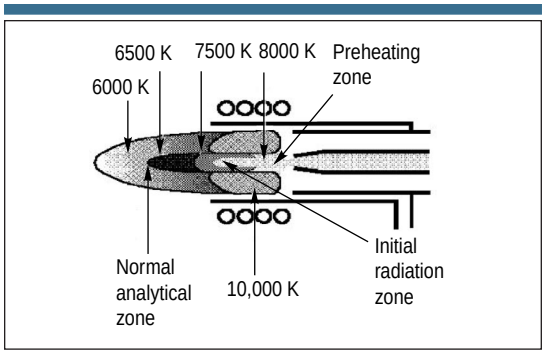

Figure 4. Different temperature zones in the plasma.

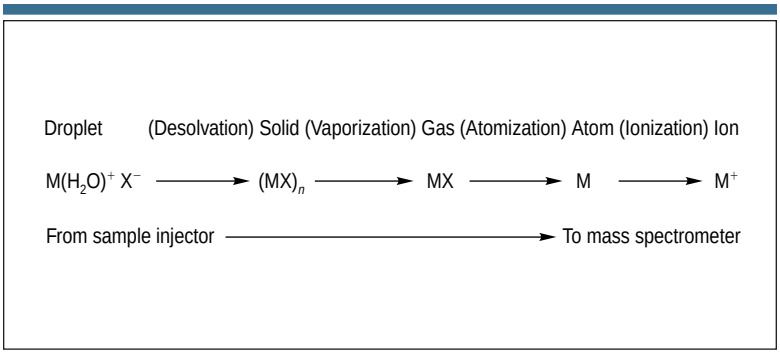

Figure 5. Mechanism of conversion of a droplet to a positive ion in the ICP.

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 conceptionally 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. Because 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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Robert Thomas *is the principal of his own freelance writing and scientific marketing consulting company, Scientific Solutions, based in Gaithersburg, MD. He specializes in trace-element analysis and can be contacted by e-mail at thomasrj@bellatlantic.net or via his web site at www.scientificsolutions1.com.* ◆

A Beginner's Guide to ICP-MS

Part IV: The Interface Region

ROBERT THOMAS

The interface region is probably the most critical area of the whole inductively coupled plasma mass spectrometry (ICP-MS) system. It certainly gave the early pioneers of the technique the most problems to overcome. Although we take all the benefits of ICP-MS for granted, the process of taking a liquid sample, generating an aerosol that is suitable for ionization in the plasma, and then sampling a representative number of analyte ions, transporting them through the interface, focusing them via the ion optics into the mass spectrometer, finally ending up with detection and conversion to an electronic signal, are not trivial tasks. Each part of the journey has its own unique problems to overcome but probably the most challenging is the movement of the ions from the plasma to the mass spectrometer. Let's begin by explaining how the ion-sampling process works, which will give readers an insight into the many problems faced by the early researchers.

SAMPLING THE IONS

Figure 1 shows the proximity of the interface region to the rest of the instrument. The role of the interface is to transport the ions efficiently, consistently, and with electrical integrity from the plasma, which is at atmospheric pressure (760 Torr), to the mass spectrometer analyzer region, which is at approximately 10^{-6} Torr. One first achieves this by directing the ions into the interface region. The interface consists of two metallic cones with very small orifices, which are maintained at a vacuum of ~2 Torr with a mechanical roughing pump. After the ions are generated in the plasma, they pass through the first cone, known as the sampler cone, which has an orifice diameter of 0.8–1.2 mm. From there they travel a short distance to the skimmer cone, which is generally sharper than the sampler cone and has a much smaller orifice (0.4–0.8 mm i.d.). Both cones are usually made of nickel, but they can be made of materials such as platinum that are far more tolerant to corrosive liquids. To reduce the effects of the high-temperature plasma on the cones, the interface housing is water-cooled and made from a material that dissipates heat easily, such as copper or aluminum. The ions then emerge from the skimmer cone, where they are directed through the ion optics, and finally are guided into the mass separation device. Figure 2 shows the interface region in greater detail; Figure 3 shows a close-up of the sampler and skimmer cones.

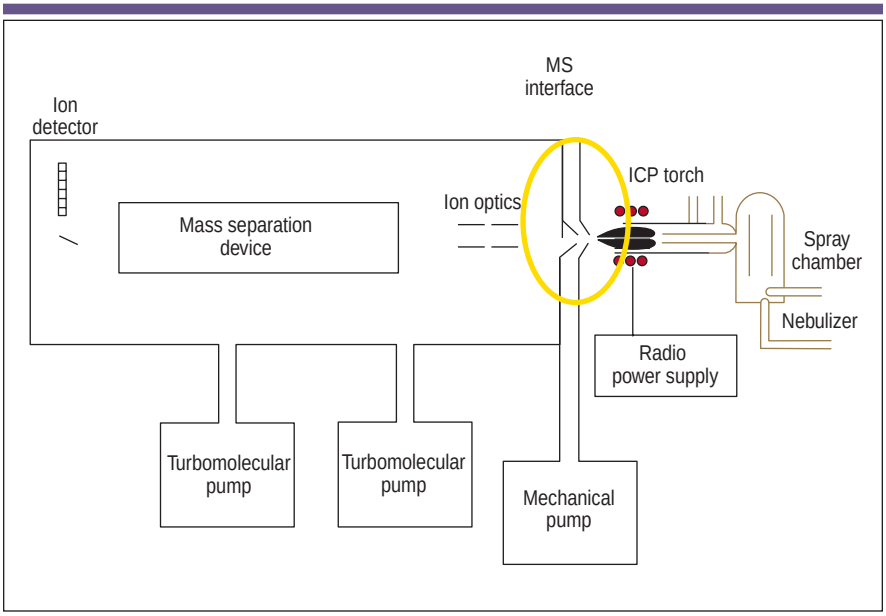

Figure 1. Schematic of an inductively coupled plasma mass spectrometry (ICP-MS) system, showing the proximity of the interface region.

CAPACITIVE COUPLING

This process sounds fairly straightforward but proved very problematic during the early development of ICP-MS because of an undesired electrostatic (capacitive) coupling between the load coil and the plasma discharge, producing a potential difference of 100–200 V. Although this potential is a physical characteristic of all inductively coupled plasma discharges, it is particularly serious in an ICP mass spectrometer because the capacitive coupling creates an electrical discharge between the plasma and the sampler cone. This discharge, commonly called the pinch effect or secondary discharge, shows itself as arcing in the region where the plasma is in contact with the sampler cone (1). This process is shown very simplistically in Figure 4.

If not taken care of, this arcing can cause all kinds of problems, including an increase in doubly charged interfering species, a wide kinetic energy spread of sampled ions, formation of ions gener-

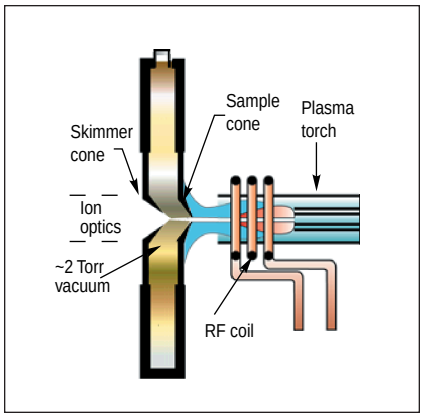

Figure 2. Detailed view of the interface region.

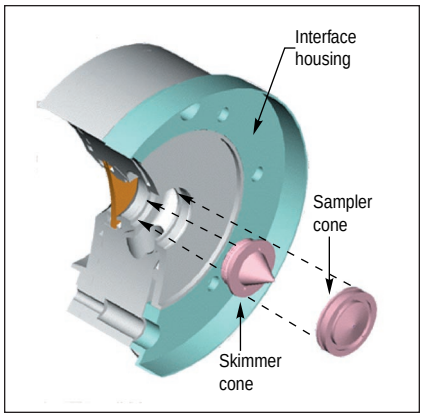

Figure 3. Close-up view of the sampler and skimmer cones. (Courtesy PerkinElmer Instruments, Norwalk, CT.)

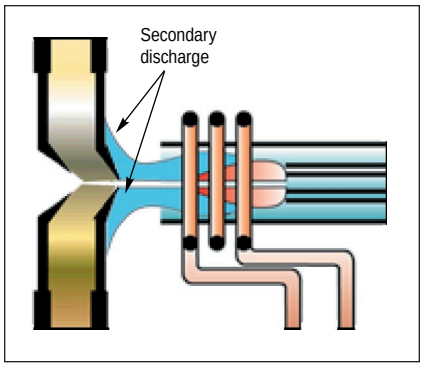

Figure 4. Interface area affected by secondary discharge.

ated from the sampler cone, and a decreased orifice lifetime. These problems were reported by many of the early researchers of the technique (2, 3). In fact, because the arcing increased with sampler cone orifice size, the source of the secondary discharge was originally thought to be the result of an electro-gas-dynamic effect, which produced an increase in electron density at the orifice (4). After many experiments it was eventually realized that the secondary discharge was a result of electrostatic coupling of the load coil to the plasma. The problem was first eliminated by grounding the induction coil at the center, which had the effect of reducing the radio frequency (RF) potential to a few volts. This effect can be seen in Figure 5, taken from one of the early papers, which shows the reduction in plasma potential as the coil is grounded at different positions (turns) along its length.

Originally, the grounding was implemented by attaching a physical grounding strap from the center turn of the coil to the interface housing. In today's instrumentation the grounding is achieved in a number of different ways, depending on the design of the interface. Some of the most popular designs include balancing the oscillator inside the circuitry of the RF generator (5); positioning a grounded shield or plate between the coil and the plasma torch (6); or using two interlaced coils where the RF fields go in opposing directions (7). They all work differently but achieve a similar result of reducing or eliminating the secondary discharge.

ION KINETIC ENERGY

The impact of a secondary discharge cannot be overestimated with respect to its effect on the kinetic energy of the ions being sampled. It is well documented that the energy spread of the ions entering the mass spectrometer must be as low as possible to ensure that they can all be focused efficiently and with full electrical integrity by the ion optics and the mass separation device. When the ions emerge from the argon plasma, they will all have different kinetic energies based on their mass-to-change ratio. Their velocities should all be similar because they are controlled by rapid expansion of the bulk plasma, which will be neutral as long as it is maintained at zero potential. As the ion beam passes through the sampler cone into the skimmer cone, expansion will take place, but its composition and integrity will be maintained, assuming the plasma is neutral. This can be seen in Figure 6.

Electrodynamic forces do not play a role as the ions enter the sampler or the skimmer because the distance over which the ions exert an influence on each other (known as the *Debye length*) is small (typically 10^{-3}–10^{-4} mm) compared with the diameter of the orifice (0.5–1.0 mm) (8), as Figure 7 shows.

It is therefore clear that maintaining a neutral plasma is of paramount importance to guarantee electrical integrity of the ion beam as it passes through the interface region. If a secondary discharge is present, it changes the electrical characteristics of the plasma, which will affect the kinetic energy of the ions differently, depending on their mass. If the plasma is at zero potential, the ion energy spread is in the order of 5–10 eV. However, if a secondary discharge is present, it results in a much wider spread of ion energies entering the mass spectrometer (typically 20–40 eV), which makes ion focusing far more complicated (8).

BENEFITS OF A WELL-DESIGNED INTERFACE

The benefits of a well-designed interface are not readily obvious if simple aqueous samples are analyzed using only one set of operating conditions. However, it becomes more apparent when many different sample types are being analyzed, requiring different operating parameters. A true test of the design of the interface occurs when plasma conditions need to be changed, when the sample matrix changes, or when a dry sample aerosol is being introduced into the ICP-MS. Analytical scenarios like these have the potential to induce a secondary discharge, change the kinetic energy of the ions entering the mass spectrometer, and affect the tuning of the ion optics. It is therefore

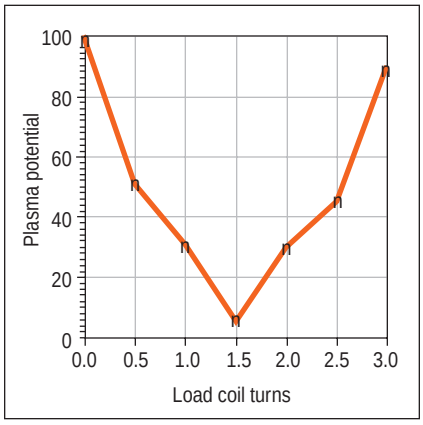

Figure 5. Reduction in plasma potential as the load coil is grounded at different positions (turns) along its length.

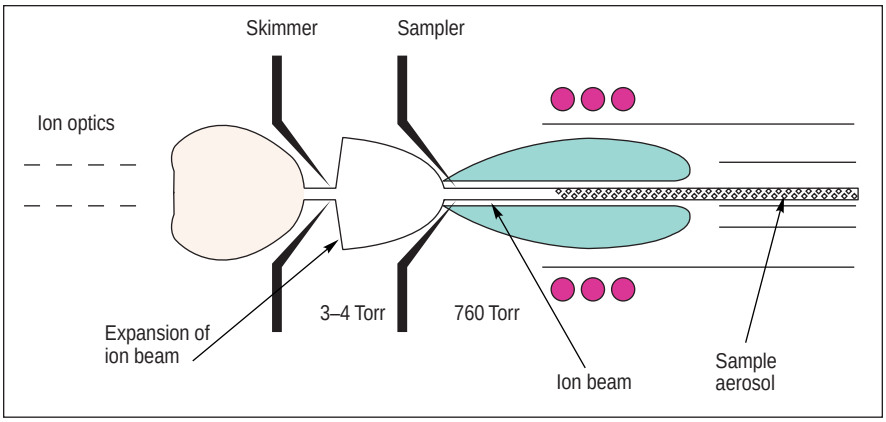

Figure 6. The composition of the ion beam is maintained, assuming a neutral plasma.

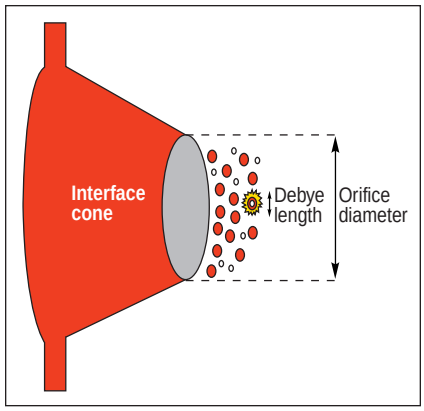

Figure 7. Electrodynamic forces do not affect the composition of the ion beam entering the sampler or the skimmer cone.

critical that the interface grounding mechanism can handle these types of real-world applications, of which typical examples include

• The use of cool-plasma conditions. It is standard practice today to use cool-plasma conditions (500–700 W power and 1.0–1.3 L/min nebulizer gas flow) to lower the plasma temperature and reduce argon-based polyatomic interferences such as $^{40}Ar^{16}O$, ^{40}Ar, and ^{38}ArH, in the determination of difficult elements like ^{56}Fe, ^{40}Ca, and ^{39}K. Such dramatic changes from normal operating conditions (1000 W, 0.8 L/min) will affect the electrical characteristics of the plasma.

• Running volatile organic solvents. Analyzing oil or organic-based samples requires a chilled spray chamber (typically −20 °C) or a membrane desolvation system to reduce the solvent loading on the plasma. In addition, higher RF power (1300–1500 W) and lower nebulizer gas flow (0.4–0.8 L/min) are required to dissociate the organic components in the sample. A reduction in the amount of solvent entering the plasma combined with higher power and lower nebulizer gas flow translate into a hotter plasma and a change in its ionization mechanism.

• Reducing oxides. The formation of oxide species can be problematic in some sample types. For example, in geochemical applications it is quite common to sacrifice sensitivity by lowering the nebulizer gas flow and increasing the RF power to reduce the formation of rare earth oxides, which can interfere spectrally with the determination of other analytes. Unfortunately these conditions have the potential to induce a secondary discharge.

• Running a "dry" plasma. Sampling accessories such as membrane desolvators, laser ablation systems, and electrothermal vaporization devices are being used more routinely to enhance the flexibility of ICP-MS. The major difference between these sampling devices and a conventional liquid sample introduction system, is that they generate a "dry" sample aerosol, which requires totally different operating conditions compared with a conventional "wet" plasma. An aerosol containing no solvent can have a dramatic effect on the ionization conditions in the plasma.

Even though most modern ICP-MS interfaces have been designed to minimize the effects of the secondary discharge, it

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"Tutorial" continued from page 34

shouldn't be taken for granted that they can all handle changes in operating conditions and matrix components with the same amount of ease. The most noticeable problems that have been reported include spectral peaks of the cone material appearing in the blank (9); erosion or discoloration of the sampling cones; widely different optimum plasma conditions for different masses (10); and increased frequency of tuning the ion optics (8). Of all these, probably the most inconvenient problem is regular optimization of the lens voltages, because slight changes in plasma conditions can produce significant changes in ion energies, which require regular retuning of the ion optics. Even though most instruments have computer-controlled ion optics, it becomes another variable that must be optimized. This isn't a major problem but might be considered an inconvenience for a high–sample throughput lab. There is no question that the plasma discharge, interface region, and ion optics all have to be designed in concert to ensure that the instrument can handle a wide range of operating conditions and sample types. The role of the ion optics will be discussed in greater detail in the next installment of this series.

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Robert Thomas *has more than 30 years experience in trace element analysis. He is the principal of his own freelance writing and scientific consulting company, Scientific Solutions, based in Gaithersburg, MD. He can be contacted by e-mail at thomasrj@bellatlantic.net or via his web site at www.scientificsolutions1.com.*◆

A Beginner's Guide to ICP-MS

Part V: The Ion Focusing System

ROBERT THOMAS

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.

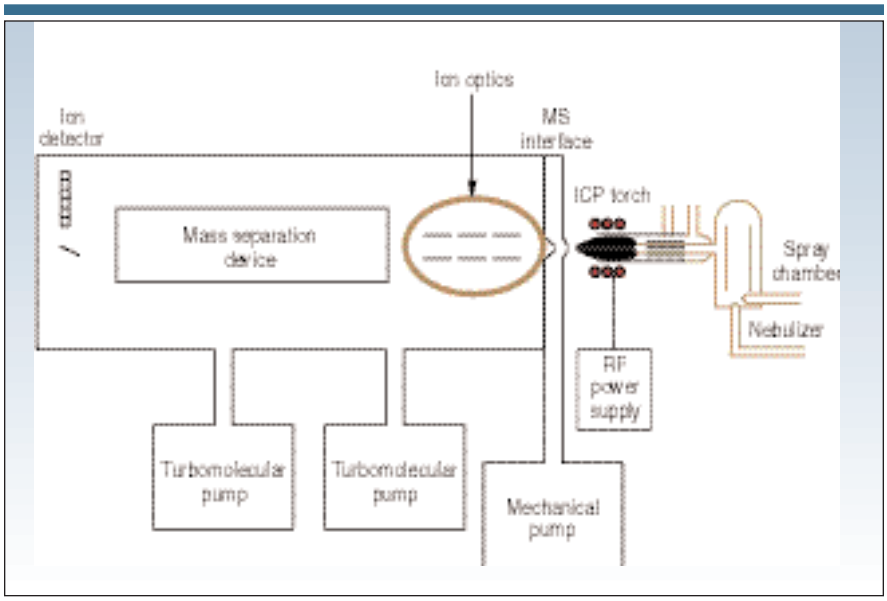

Figure 1. Position of ion optics relative to the plasma torch and interface region.

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-

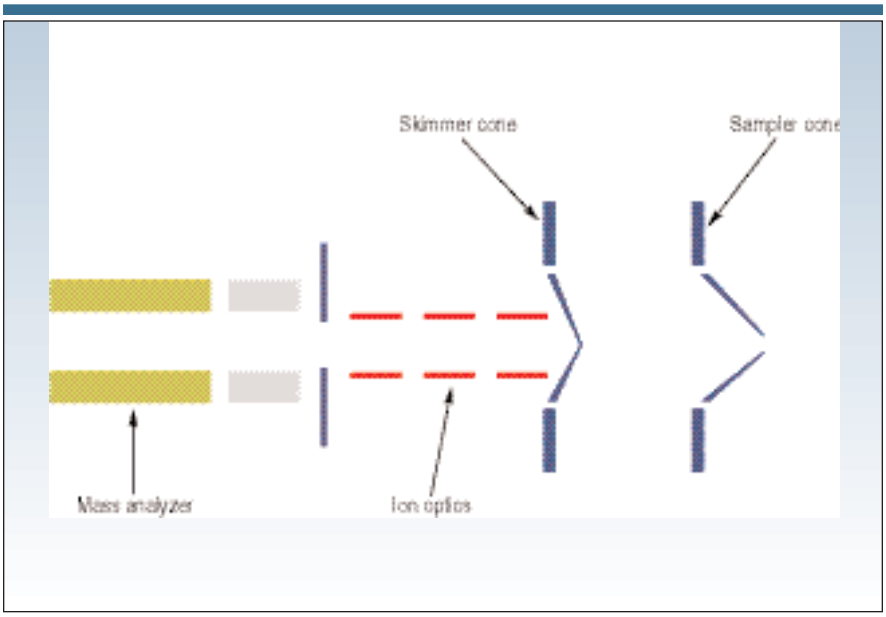

Figure 2. A generic ion focusing system, showing position of ion optics relative to the interface cones and mass analyzer.

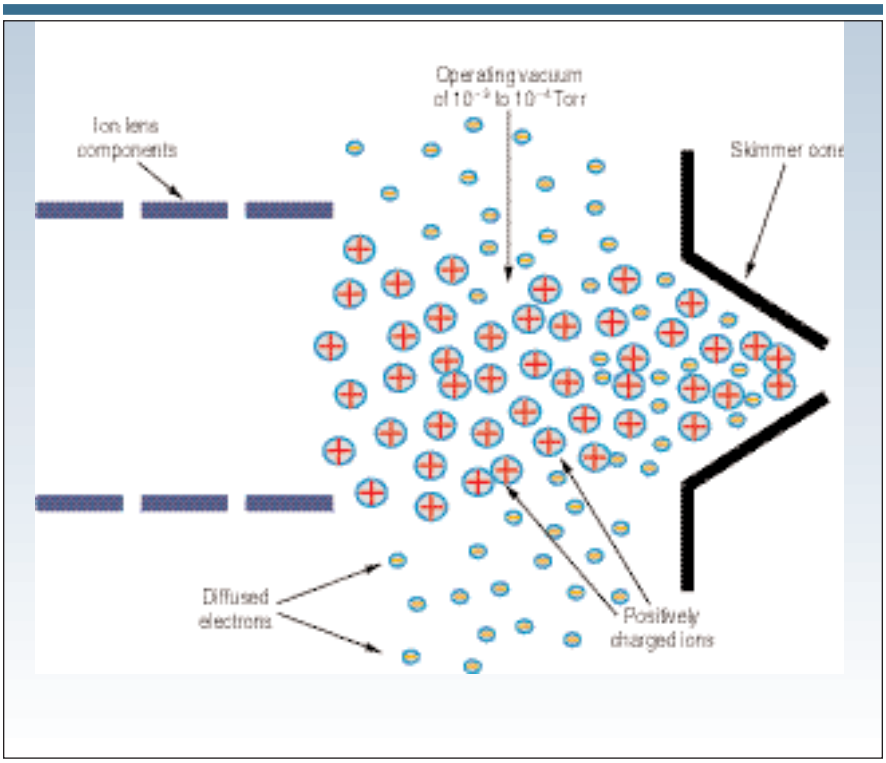

Figure 3. Extreme pressure drop in the ion optic chamber produces diffusion of electrons, resulting in a positively charged ion beam.

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 electrodynamics. 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

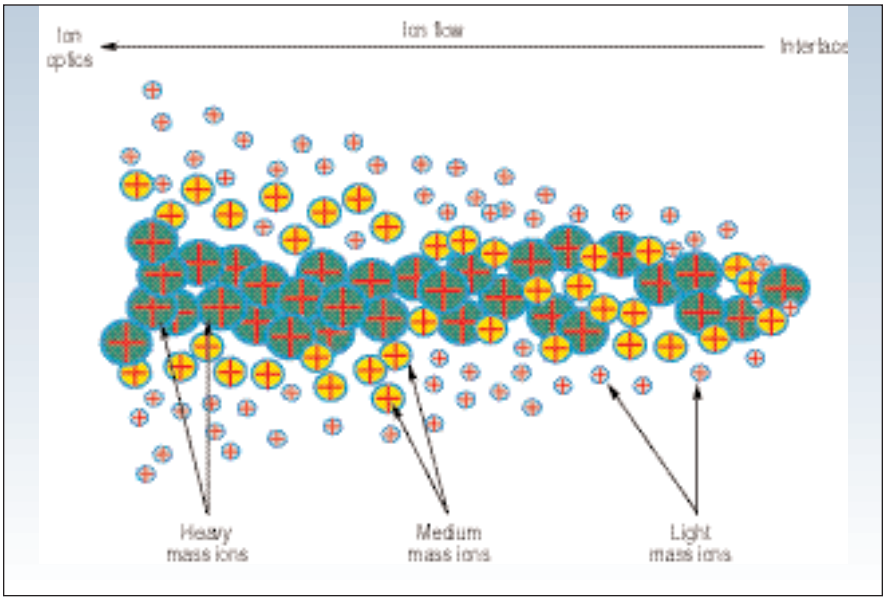

Figure 4. The degree of ion repulsion will depend on kinetic energy of the ions: those with high kinetic energy (green with red +) will be transmitted in preference to ions with medium (yellow with red +) or low kinetic energy (blue with red +).

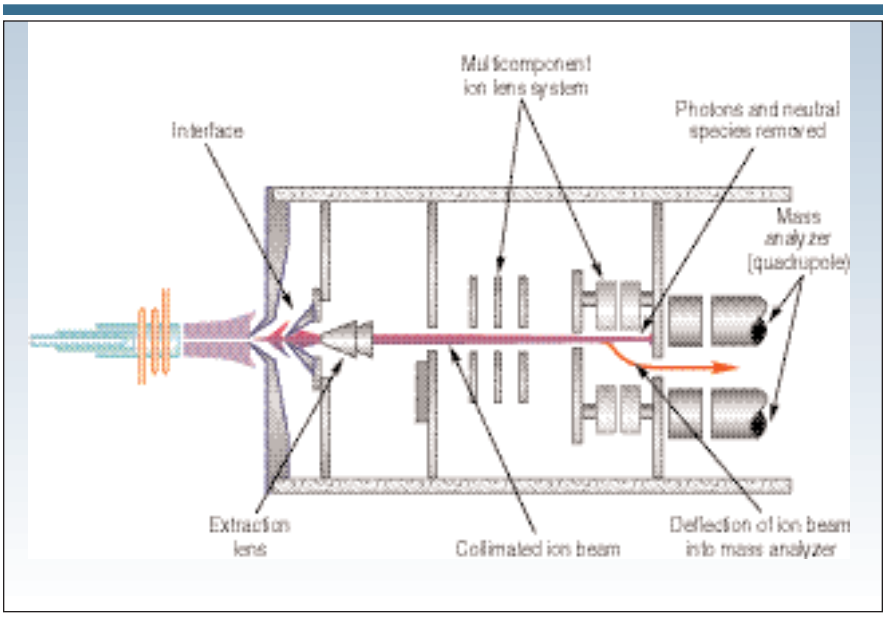

Figure 5. Schematic of a multicomponent lens system with extraction lens and off-axis quadrupole mass analyzer (courtesy of Agilent Technologies [Wilmington, DE]).

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

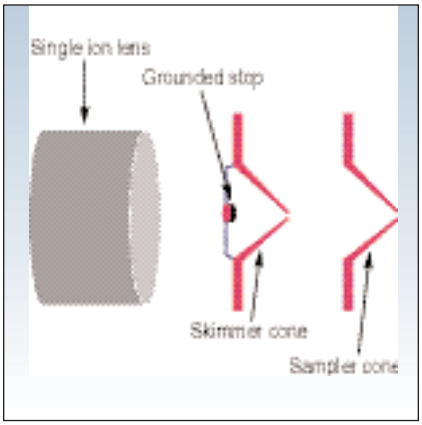

Figure 6. Schematic of a single ion lens and grounded stop system (not to scale [courtesy of PerkinElmer Instructs {Norwalk, CT}]).

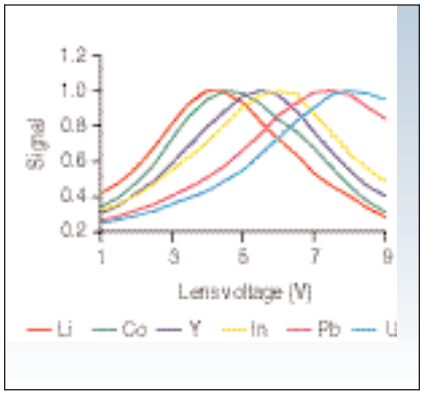

Figure 7. A calibration of optimum lens voltages is used to ramp-scan the ion lens in concert with the mass scan of the analyzer. The signals have been normalized for comparison purposes.

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.* 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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Robert Thomas *has more than 30 years experience in trace element analysis. He is the principal of his own freelance writing and scientific consulting company, Scientific Solutions, based in Gaithersburg, MD. He can be contacted by e-mail at thomasrj@bellatlantic.net or via his web site at www.scientificsolutions1.com.*◆

Beginner's Guide to ICP-MS

Part VI — The Mass Analyzer

ROBERT THOMAS

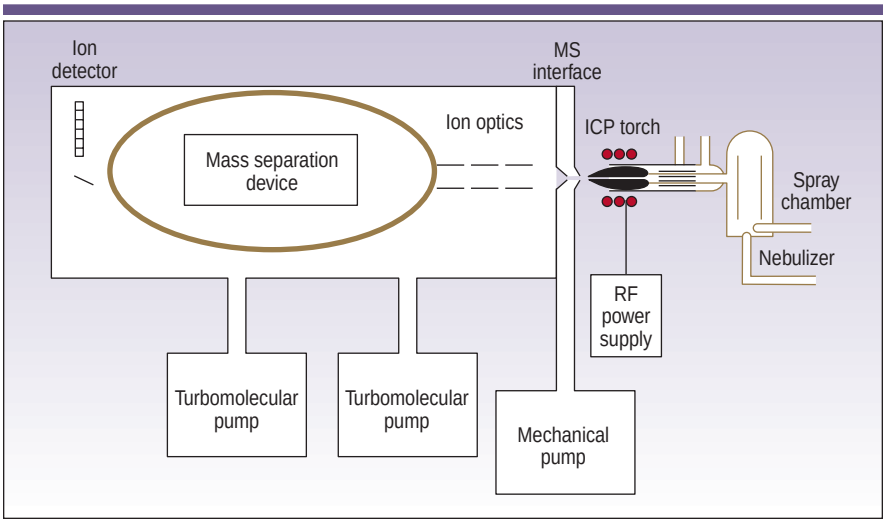

Figure 1. Schematic of an ICP-MS system showing the location of the mass separation device.

Part VI of the series on inductively coupled plasma–mass spectroscopy (ICP-MS) fundamentals deals with the heart of the system — the mass separation device. Sometimes called the mass analyzer, it is the region of the ICP mass spectrometer that separates the ions according to their mass-to-charge ratio (m/z). This selection process is achieved in a number of different ways, depending on the mass separation device, but they all have one common goal: to separate the ions of interest from all the other nonanalyte, matrix, solvent, and argon-based ions.

Although inductively coupled plasma–mass spectroscopy (ICP-MS) was commercialized in 1983, the first 10 years of its development primarily used traditional quadrupole mass filter technology to separate the ions of interest. These worked exceptionally well for most applications but proved to have limitations in determining difficult elements or dealing with more-complex sample matrices. This led to the development of alternative mass separation devices that pushed the capabilities of ICP-MS so it could be used for more challenging applications. Before we discuss these different mass spectrometers in greater detail, let's take a look at the location of the mass analyzer in relation to the ion optics and the detector. Figure 1 shows this in greater detail.

As we can see, the mass analyzer is positioned between the ion optics and the detector and is maintained at a vacuum of approximately 10^{-6} Torr with a second turbomolecular pump. Assuming the ions are emerging from the ion optics at the optimum kinetic energy (1), they are ready to be separated according to their mass-to-charge ratio by the mass analyzer. There are basically four kinds of commercially available mass analyzers: quadrupole mass filters, double focusing magnetic sector, time-of-flight, and collision–reaction cell technology. They all have their own strengths and weaknesses, which we will discuss in greater detail in the next few installments of this column. Let's first begin with the most common of the mass separation devices used in ICP-MS, the quadrupole mass filter.

QUADRUPOLE MASS FILTER TECHNOLOGY

Developed in the early 1980s, quadrupole-based systems represent approximately 90% of all ICP mass spectrometers used today. This design was the first to be commercialized; as a result, today's quadrupole ICP-MS technology is considered a very mature, routine, high-throughput, trace-element technique. A quadrupole consists of four cylindrical or hyperbolic metallic rods of the same length and diameter. They are typically made of stainless steel or molybdenum, and sometimes have a ceramic coating for corrosion resistance. Quadrupoles used in ICP-MS are typically 15–20 cm in length and about 1 cm in diameter and operate at a frequency of 2–3 MHz.

BASIC PRINCIPLES OF OPERATION

By placing a direct current (dc) field on one pair of rods and a radio frequency (rf) field on the opposite pair, ions of a selected mass are allowed to pass through the rods to the detector, while the others are ejected from the quadrupole. Figure 2 shows this in greater detail.

In this simplified example, the analyte ion (black) and four other ions (colored) have arrived at the entrance to the four rods of the quadrupole. When a particular rf-dc voltage is applied to the rods, the positive or negative bias on the rods will electrostatically steer the analyte ion of interest down the middle of the four rods to the end, where it will emerge and be converted to an electrical pulse by the detector. The other ions of different mass-to-charge ratios will pass through the spaces between the rods and be ejected

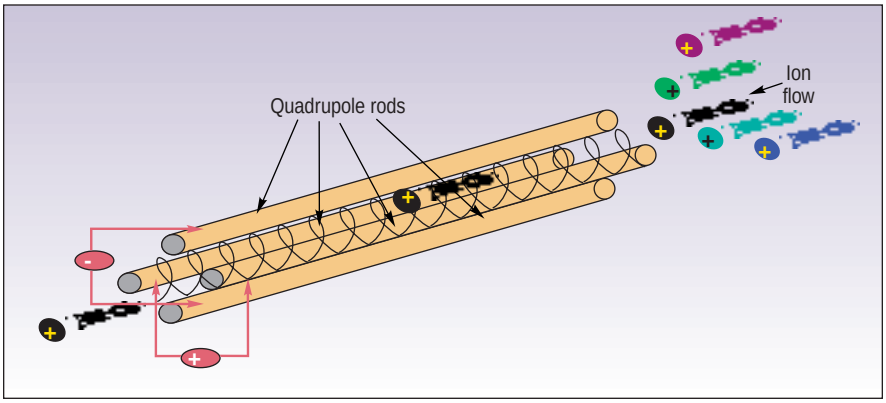

Figure 2. Schematic showing principles of a quadrupole mass filter.

from the quadrupole. This scanning process is then repeated for another analyte at a completely different mass-to-charge ratio until all the analytes in a multielement analysis have been measured. The process for the detection of one particular mass in a multielement run is represented in Figure 3. It shows a ^{63}Cu ion emerging from the quadrupole and being converted to an electrical pulse by the detector. As the rf-dc voltage of the quadrupole — corresponding to ^{63}Cu — is repeatedly scanned, the ions as electrical pulses are stored and counted by a multichannel analyzer. This multichannel data-acquisition system typically has 20 channels per mass, and as the electrical pulses are counted in each channel, a profile of the mass is built up over the 20 channels, corresponding to the spectral peak of ^{63}Cu. In a multielement run, repeated scans are made over the entire suite of analyte masses, as opposed to just one mass represented in this example.

Quadrupole scan rates are typically on the order of 2500 atomic mass units (amu) per second and can cover the entire mass range of 0–300 amu in about 0.1 s. However, real-world analysis speeds are much slower than this, and in practice 25 elements can be determined in duplicate with good precision in 1–2 min.

QUADRUPOLE PERFORMANCE CRITERIA

Two very important performance specifications of a mass analyzer govern its ability to separate an analyte peak from a spectral interference. The first is resolv-

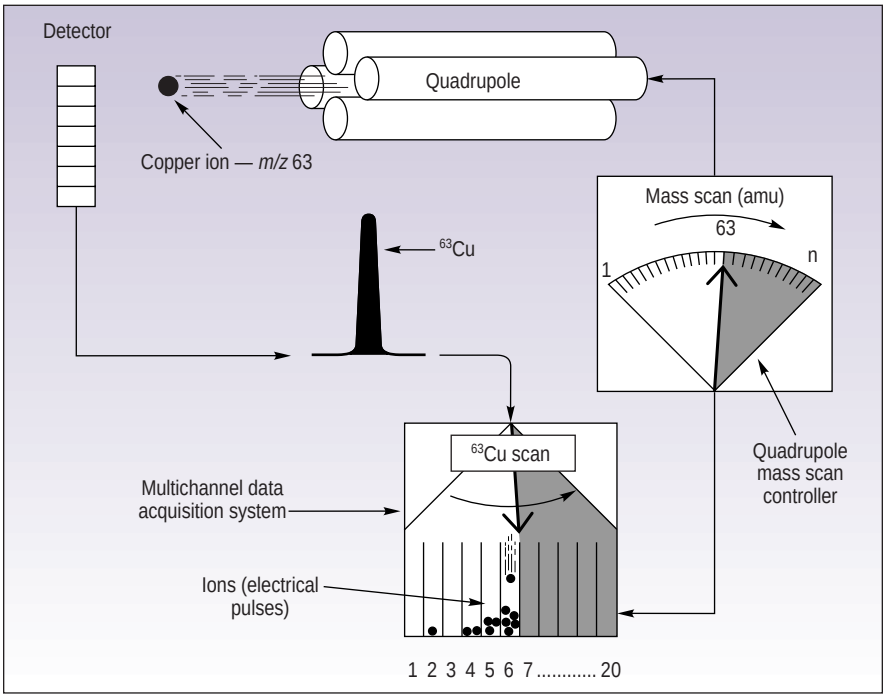

Figure 3. Profiles of different masses are built up using a multichannel data acquisition system.

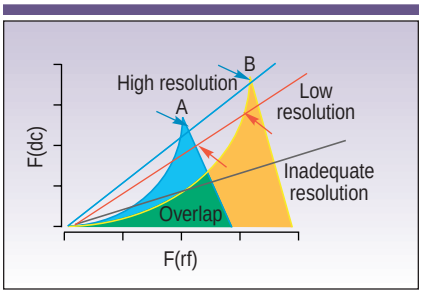

Figure 4. Simplified Mathieu stability diagram of a quadrupole mass filter, showing separation of two different masses, *A* (light blue plot) and *B* (yellow plot).

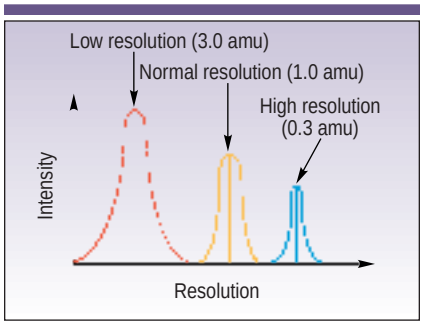

Figure 5. Sensitivity comparison of a quadrupole operated at 3.0, 1.0, and 0.3 amu resolution (measured at 10% of its peak height).

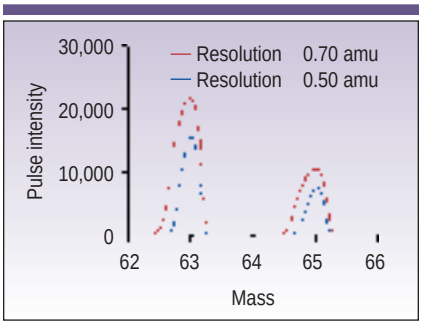

Figure 6. Sensitivity comparison of two copper isotopes, ^{63}Cu and ^{65}Cu, at resolution settings of 0.70 and 0.50 amu.

ing power (R), which in traditional mass spectrometry is represented by the following equation: $R = m/\Delta m$, where m is the nominal mass at which the peak occurs and Δm is the mass difference between two resolved peaks (2). However, for quadrupole technology, the term *resolution* is more commonly used, and is normally defined as the width of a peak at 10% of its height. The second specification is abundance sensitivity, which is the signal contribution of the tail of an adjacent peak at one mass lower and one mass higher than the analyte peak (3). Even though they are somewhat related and both define the quality of a quadrupole, the abundance sensitivity is probably the most critical. If a quadrupole has good resolution but poor abundance sensitivity, it will often prohibit the measurement of an ultratrace analyte peak next to a major interfering mass.

RESOLUTION

Let us now discuss this area in greater detail. The ability to separate different masses with a quadrupole is determined by a combination of factors including shape, diameter, and length of the rods, frequency of quadrupole power supply, operating vacuum, applied rf-dc voltages, and the motion and kinetic energy of the ions entering and exiting the quadrupole. All these factors will have a direct impact on the stability of the ions as they travel down the middle of the rods and thus the quadrupole's ability to separate ions of differing mass-to-charge ratios. This is represented in Figure 4, which shows a simplified version of the Mathieu mass stability plot of two separate masses (*A* and *B*) entering the quadrupole at the same time (4).

Any of the rf-dc conditions shown under the light blue plot will allow only mass *A* to pass through the quadrupole, while any combination of rf-dc voltages under the yellow plot will allow only mass *B* to pass through the quadrupole. If the slope of the rf-dc scan rate is steep, represented by the light blue line (high resolution), the spectral peaks will be narrow, and masses *A* and *B* will be well separated (equivalent to the distance between the two blue arrows). However, if the slope of the scan is shallow, represented by the red line (low resolution), the spectral peaks will be wide, and masses *A* and *B* will not be so well separated (equivalent to the distance between the two red arrows). On the other hand, if the slope of the scan is too shallow, represented by the gray line (inadequate resolution), the peaks will overlap each other (shown by the green area of the plot) and the masses will pass through the quadrupole without being separated. In theory, the resolution of a quadrupole mass filter can be varied between 0.3 and 3.0 amu. How-

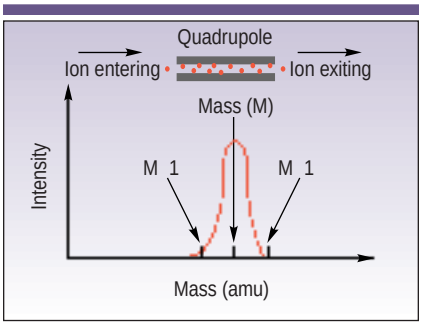

Figure 7. Ions entering the quadrupole are slowed down by the filtering process and produce peaks with a pronounced tail or shoulder at the low-mass end.

ever, improved resolution is always accompanied by a sacrifice in sensitivity, as seen in Figure 5, which shows a comparison of the same mass at a resolution of 3.0, 1.0, and 0.3 amu.

We can see that the peak height at 3.0 amu is much larger than the peak height at 0.3 amu but, as expected, it is also much wider. This would prohibit using a resolution of 3.0 amu with spectrally complex samples. Conversely, the peak width at 0.3 amu is very narrow, but the sensitivity is low. For this reason, a compromise between peak width and sensitivity usually has to be reached, depending on the application. This can clearly be seen in Figure 6, which shows a spectral overlay of two copper isotopes — ^{63}Cu and ^{65}Cu — at resolution settings of 0.70 and 0.50 amu. In practice, the quadrupole is normally operated at a resolution of 0.7–1.0 amu for most applications.

It is worth mentioning that most quadrupoles are operated in the first stability region, where resolving power is typically ~400. If the quadrupole is operated in the second or third stability regions, resolving powers of 4000 (5) and 9000 (6), respectively, have been achieved. However, improving resolution using this approach has resulted in a significant loss of signal. Although there are ways of improving sensitivity, other problems have been encountered, and as a result, to date there are no commercial instruments available based on this design.

Some instruments can vary the peak width *on-the-fly*, which means that the resolution can be changed between 3.0 and 0.3 amu for every analyte in a multielement run. For some challenging applications this can be beneficial, but in reality they are rare. So, even though quadrupoles can be operated at higher resolution (in the first stability region), until now the slight improvement has not become a practical benefit for most routine applications.

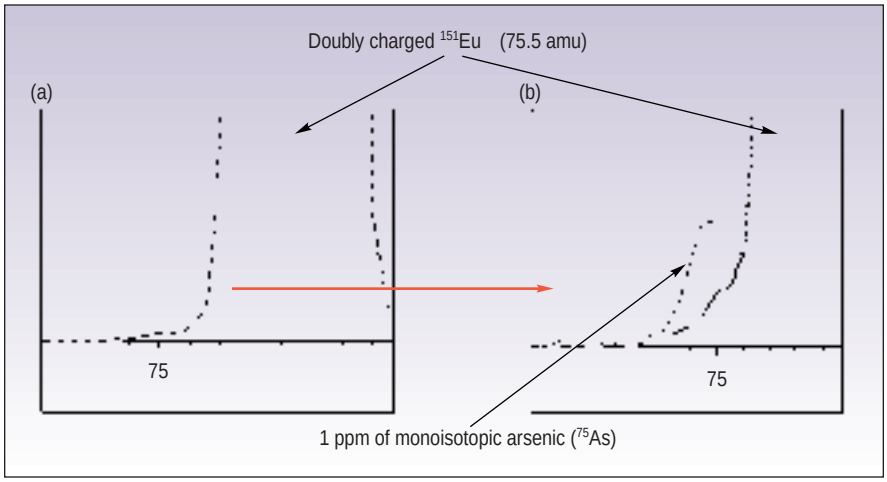

Figure 8. A low abundance sensitivity specification is critical to minimize spectral interferences, as shown by (a) a spectral scan of 50 ppm of $^{151}Eu^{++}$ at 75.5 amu and (b) an expanded view, which shows how the tail of the $^{151}Eu^{++}$ elevates the spectral background of 1 ppb of As at mass 75.

ABUNDANCE SENSITIVITY

We can see in Figure 6 that the tails of the spectral peaks drop off more rapidly at the high mass end of the peak compared with the low mass end. The overall peak shape, particularly its low mass and high mass tail, is determined by the abundance sensitivity of the quadrupole,

which is affected by a combination of factors including design of the rods, frequency of the power supply, and operating vacuum (7). Even though they are all important, probably the biggest impacts on abundance sensitivity are the motion and kinetic energy of the ions as they enter and exit the quadrupole. If one looks at the Mathieu stability plot in Figure 3, it can be seen that the stability boundaries of each mass are less defined (not so sharp) on the low mass side than they are on the high mass side (4). As a result, the characteristics of ion motion at the low mass boundary is different from the high mass boundary and is therefore reflected in poorer abundance sensitivity at the low mass side compared with the high mass side. In addition, the velocity (and therefore the kinetic energy) of the ions entering the quadrupole will affect the ion motion and, as a result, will have a direct impact on the abundance sensitivity. For that reason, factors that affect the kinetic energy of the ions, like high plasma potential and the use of lens components to accelerate the ion beam, will degrade the instrument's abundance sensitivity (8).

These are the fundamental reasons why the peak shape is not symmetrical with a quadrupole and explains why there is always a pronounced shoulder at the low mass side of the peak compared to the high mass side — as represented in Figure 7, which shows the theoretical peak shape of a nominal mass M. We can see that the shape of the peak at one mass lower (M − 1) is slightly different from the other side of the peak at one mass higher (M + 1) than the mass M. For this reason, the abundance sensitivity specification for all quadrupoles is always worse on the low mass side than on the high mass side and is typically 1×10^{-6} at M − 1 and 1×10^{-7} at M + 1. In other words, an interfering peak of 1 million counts per second (cps) at M − 1 would produce a background of 1 cps at M, while it would take an interference of 10^7 cps at M + 1 to produce a background of 1 cps at M.

BENEFITS OF GOOD ABUNDANCE SENSITIVITY

Figure 8 shows an example of the importance of abundance sensitivity. Figure 8a is a spectral scan of 50 ppm of the doubly charged europium ion — $^{151}Eu^{++}$ at 75.5 amu (a doubly charged ion is one with two positive charges, as opposed to a normal singly charged positive ion, and exhibits a *m/z* peak at half its mass). We can see that the intensity of the peak is so great that its tail overlaps the adjacent mass at 75 amu, which is the only available mass for the determination of arsenic. This is highlighted in Figure 8b, which shows an expanded view of the tail of the $^{151}Eu^{++}$, together with a scan of 1 ppb of As at mass 75. We can see very clearly that the ^{75}As signal lies on the sloping tail of the $^{151}Eu^{++}$ peak. Measurement on a sloping background like this would result in a significant degradation in the arsenic detection limit, particularly as the element is monoisotopic and no alternative mass is available. This example shows the importance of a low abundance sensitivity specification in ICP-MS.

DIFFERENT QUARDUPOLE DESIGNS

Many different designs of quadrupole are used in ICP-MS, all made from different materials with various dimensions, shapes, and physical characteristics. In addition, they are all maintained at slightly different vacuum chamber pressures and operate at different frequencies. Theory tells us that hyperbolic rods should generate a better hyperbolic (elliptical) field than cylindrical rods, resulting in higher transmission of ions at higher resolution. It also tells us that a higher operating frequency means a higher rate of oscillation — and therefore separation — of the ions as they travel down the quadrupole. Finally, it is very well accepted that a higher vacuum produces fewer collisions between gas molecules and ions, resulting in a narrower spread in kinetic energy of the ions and therefore less of a tail at the low mass side of a peak. However, given all these specification differences, in practice the performance of most modern quadrupole ICP-MS instrumentation is very similar.

So even though these differences will mainly be transparent to users, there are some subtle variations in each instrument's measurement protocol and the software's approach to peak quantitation. This is a very important area that we will discuss it in greater detail in a future column. The next part of the series will continue with describing the fundamental principles of other types of mass analyzers used in ICP-MS.

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Robert Thomas *has more than 30 years experience in trace element analysis. He is the principal of his own freelance writing and scientific consulting company, Scientific Solutions, based in Gaithersburg, MD. He can be contacted by e-mail at thomasrj@bellatlantic.net or via his web site at www.scientificsolutions1.com.*◆