A Beginner’s Guide to ICP-MS

Part I

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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.
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 2.** Simplified schematic of a chromium ground-state atom (Cr⁰).

**Figure 3.** Conversion of a chromium ground-state atom (Cr⁰) to an ion (Cr⁺).
Table I. Breakdown of the atomic structure of copper isotopes.

<table>
<thead>
<tr>
<th></th>
<th>$^{63}\text{Cu}$</th>
<th>$^{65}\text{Cu}$</th>
</tr>
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<tbody>
<tr>
<td>Protons ($p^+$)</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>Electrons ($e^-$)</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>Neutrons ($n$)</td>
<td>34</td>
<td>36</td>
</tr>
<tr>
<td>Atomic mass ($p^+ + n$)</td>
<td>63</td>
<td>65</td>
</tr>
<tr>
<td>Atomic number ($p^+$)</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>Natural abundance</td>
<td>69.17%</td>
<td>30.83%</td>
</tr>
<tr>
<td>Nominal atomic weight</td>
<td>63.55*</td>
<td></td>
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</tbody>
</table>

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

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

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 sub-shells, 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.

REFERENCES


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

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

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

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

**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 minrollers that rotate at the same speed. The constant motion and pressure of the rollers on the pump tubing feed the sample to the nebulizer. 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% 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
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.
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.

REFERENCES
(2) B. L. Sharp, Analytical Atomic Spectrometry 3, 613 (1980).

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

Inductively coupled plasmas are by far the most common type of plasma sources used in today’s commercial ICP–optical emission spectrometry (OES) and ICP-MS instrumentation. However, it wasn’t always that way. In the early days, when researchers were attempting to find the ideal plasma source to use for spectrometric studies, it was unclear which approach would prove to be the most successful. In addition to ICPs, some of the other novel plasma sources developed were direct current plasmas (DCP) and microwave-induced plasmas (MIP). A DCP is formed when a gas (usually argon) is introduced into a high current flowing between two or three electrodes. Ionization of the gas produces an inverted Y-shaped plasma. Unfortunately, early DCP instrumentation was prone to interference effects and also had some usability and reliability problems. For these reasons, the technique never became widely accepted by the analytical community (1). However, its one major benefit was that it could aspirate high levels of dissolved or suspended solids, because there was no restrictive sample injector for the solid material to block. This feature alone made it attractive for some laboratories, and once the initial limitations of DCPs were better understood, the technique became more accepted. In fact, for those who want a DCP excitation source coupled with an optical emission instrument today, an Echelle-based grating using a solid-state detector is commercially available (2).

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

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**Figure 4.** Different temperature zones in the plasma.

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

REFERENCES


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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.

**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-
Detailed view of the interface region.

Interface area affected by 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-charge 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...
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 $2^\circ$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...
In this month’s column we will explore why the user requirements specification (URS) and the validation plan are so important for the validation of spectrometry software, and we’ll cover the specification and system selection from a software perspective.

In the first installment of this series, we looked at the system development life cycle (SDLC) and some validation concepts (1). One concept was that validation is a process that covers the entire system development life cycle: Once started, you can’t stop. Now we will look in more detail at the first part of the SDLC.

THE WAY IT WAS
In the past, the spectrometer and software were purchased and then, just before they were put into operational use, someone thought about validation. Some common questions may have been:

• Have we validated the system? No.
• Does it matter? Probably.
• Will we get caught? Don’t even think about answering no to this question.

Considering validation at such a late stage of the life cycle will mean a delay in going operational, thus failing to gain benefit from the investment in the instrument or going live with no regulatory coverage. It depends on your approach to risk and if can you sleep at night.

THE WAY IT SHOULD BE
However, as we discussed in the previous article in this series, a proactive approach to validation is necessary and, if done right, will actually save you money by ensuring that you buy the right instrument for the job. So we’ll start at the beginning and look at the first stages of the life cycle:

• Defining and controlling the validation throughout the whole life cycle (writing the validation plan).
• Specifying what you want the system to do (writing a user requirements specification).
• Selecting the system using the requirements defined in the URS as the basis, rather than “the salesperson bought me a good meal.”

Defining and controlling the overall validation. The validation plan is one name for the document that controls the validation effort for your spectrometer software. However, the name for this document varies from laboratory to laboratory. It may be called the validation plan, master validation plan, validation master plan, or quality plan.

Regardless of what you call this document in your organization, it should cover all the steps you are going to take to demonstrate the quality of the spectrometry software in your laboratory.

Ideally the validation plan should be written as early as possible in the life cycle to define the overall steps that are required as well as the documents to be produced during each phase of the life cycle. There are different approaches to writing validation plans, and the document can be written in several stages in the life cycle.

I’ll outline my philosophy and rationale now and you, dear reader, can accept this as is, modify it, or ignore it.

First, you should write the validation plan as either the first or second document in the life cycle; I advise writing it after the first or second draft of the URS to incorporate any implementation or roll-out issues in the overall validation strategy. The rationale for this approach is that the validation plan provides documented evidence of intent of the validation. The document will set out the overall strategy of the validation and define the life cycle phases and the documented evidence that will be produced in each phase. If you leave writing the validation plan until later in the project, one or more phases of the life cycle will have passed and you may need to write documents retrospectively. Furthermore, you’ll be out of compliance with 21 CFR 11.10(k)(2), which requires a time-sequenced audit trail of systems documentation.

Content of a validation plan. The purpose of a validation plan is to provide documentation of intent for the whole validation, including a definition of the life cycle used, documentation to be produced during the each stage of the life cycle, and roles and responsibilities of everyone involved in the project.

To provide a better perspective, the content of a validation plan is listed in the sidebar. It is based on the Institute of Electronic and Electrical Engineers (IEEE) standard for validation and verification plans (2).

This document is important because it defines what you will do in the validation, and you will be judged against it when your operation is inspected. Therefore, read and understand it well — don’t write the plan and forget it, because what you plan does not always come to pass. Usually deviations from the plan occur that
you’ll need to record, such as documents not written, new documents required that have not been specified, or parts of the life cycle omitted or modified. These changes will need to be noted under the deviation procedure that you have in place in the plan. Noting the changes sounds like a pain, but once the principles are understood, it is relatively simple to do.

**DESIGN: THE URS**

How much money have you wasted on purchasing spectrometers that were not fit for purpose, did not do the job you wanted, or used software that was not up to snuff? From a business perspective, a document that says what you want the instrument and software to do will be beneficial, because you’ll have a better chance of selecting the right instrument and software.

From a regulatory perspective, remember that the definition of validation presented in the first part of this series (1) included that phrase “predefined specifications.” The document that provides the laboratory with the predefined specifications for the spectrometer and the software is the URS. Without this document or an equivalent, you cannot validate your spectrometer software, because you don’t have a predefined specification and therefore there is nothing to test against. This is particularly important when you consider which electronic record and electronic signature functions are pertinent to define and test for the way that you will use the instrument.

The URS provides the answer to the question, What do you want the system to do? This makes the assumption that you know what you want the system to do.

A well-written URS provides several specific benefits. For one thing, it serves as a reference against which off-the-shelf commercial products are selected and evaluated in detail and any enhancements are defined. Also, you are less likely to be seduced by technology or buy a poor system. Furthermore, the URS reduces the total system effort and costs, because careful review of the document should reveal omissions, misunderstandings, and inconsistencies in the specification. This means that they can be corrected easily before you purchase the system. Finally, a well-written URS provides the input to user acceptance test specifications and qualification of the system.

**General guidelines for a URS.** A user requirements specification clearly and precisely defines what the customer (that is, you) wants the system to do, and it should be understood by both the customer and the instrument vendor. The URS is a living document and must be updated, via a change control procedure, throughout the computer system life cycle. After purchase, when you upgrade the software, also update the URS to reflect the changes and new functions in the latest version.

A URS defines the functions to be carried out, the data on which the system will operate, and the operating environment. Ideally, the emphasis is on the required functions and not the method of implementation, as this may be the identification of a solution. The aim of a URS is to make a statement of requirements rather than a statement of a potential solution. This allows users to look objectively at software from different vendors and make an objective decision as to which system is required.

**Nature of the URS.** The URS should address the following basic issues:

• **Functionality:** What is the system or function supposed to do?

• **External interfaces:** How does the system interact with other systems and the users?

• **Performance:** What are the speed, availability, and response time of the various functions of the system?

• **Attributes:** What are the security considerations of each function?

• **Design constraints:** Must the system work on specific hardware or use an operating system, and are these consistent with your organization’s standards?

• **Prioritization:** All requirements are ranked for importance as either mandatory or desirable (respectively, you must use the system, or it would simply be nice to have it).

The URS should form the basis of the solution to be delivered by the selected vendor. If this does not happen, you can leave yourself open to a poor-quality product because either you don’t know what you want the system to do or you can’t articulate this need to the vendor.

**Writing the specification.** The following guidelines should be followed during the production of the specification:

• Each requirement statement should be uniquely referenced and no longer than 250 words.

• The URS should be consistent; therefore, requirement statements should not be duplicated or contradicted.

• The URS should express requirements and not design solutions.

• Each requirement should be testable (this allows the tests to be designed as soon as the URS is finalized).
A URS can be extensive unless you states that every requirement has only one interpretation and is clear.

- The URS should be modifiable, but requirements should be prioritized as mandatory or desirable.
- The URS should be defined in a specific section and not be avoided, and key words should be defined in a specific section in the document.

Organizing requirements: Go with the workflow. A URS can be extensive unless you plan well, so careful consideration should be given to organizing requirements in the easiest manner to understand. The best framework for writing a user requirements specification for most spectrometers is to follow the process or workflow that the data system will be automating. Therefore, if you have mapped the process, it makes an ideal prompt for the URS because the requirements can be defined against each activity in the process.

This idea of documenting what we want in sufficient detail sounds great, but it means more work, doesn’t it? Yes, that is true, but consider the benefits. The more time you spend in the specification and design phase getting your ideas and concepts right, the quicker the rest of the life cycle will go if you know what you want. You will get a spectrometer and associated software that meet your requirements more fully, and there will be less chance later in the life cycle of finding out that what looked good early on does not meet certain key requirements now.

Contrast this to selecting a spectrometer with no user requirements. (This bit should be easy, because we have all done it.)

Don’t forget the instrument specs! In this series we’ll concentrate on the software elements, but don’t forget the instrument itself. The software and the instrument must be an integrated system. So, the instrument specification also needs to be included in the overall URS. What operating requirements do you need from the spectrometer, such as mass range and resolution or wavelength? Get them down in the URS.

A specific example. Table I shows an example of what a URS could look like. It defines the requirements for audit trail functionality in the spectrometer software to meet Part 11 requirements. Looks impressive, doesn’t it? Look at the table and you’ll see that each requirement is uniquely numbered (not bad), short (good), and prioritized (getting better). However, 21 CFR 11 states that every change must not overwrite the original result and must include the name of the user, along with date and time of the change. This is not mentioned in this specification (bummer!). So be careful, specify the system, and review it carefully or something essential may be missed.

### SYSTEM SELECTION: PART ONE

Because your requirements for the overall system are contained in the URS, the document can be used as a basis to design the tests to evaluate the various systems offered by vendors. Can the systems offered meet your requirements, especially for the mandatory functions? Using the URS requirements for system selection helps ensure that the system selected matches your business needs.

Don’t forget that the tests you use for system selection should also include common problems that you know happen in your laboratory. What happens when samples are switched and you notice the error only after the analysis? Can the system handle the changes easily and with suitable audit trail entries?

The system you select will be based on the practical experience of using it in your laboratory environment. However, before you sign on the dotted line, you may want to make sure that the software was developed in a quality manner through a vendor audit.

### VENDOR CERTIFICATES AND AUDITS

Many spectrometer vendors will be certified to ISO 9000 of some description and will offer you a certificate that the system conforms to its quality processes. This is fine, but please remember that no requirement for product quality exists in any ISO 9000 schedule, and if you look at the warranty of any software product, there is no guarantee that the software is stated to be either fit for purpose or error free. The certificates are fine, but if the system is critical to your operation, my advice is to consider a vendor audit.

The vendor audit should take place once the product has been selected. The purpose is simply to see if the ISO 9000 quality system is operated effectively. The evaluation and audit process is a very important part of the life cycle, because it shows whether design, building, and testing stages (which are under the control

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**Table I: Example Specification of Audit Trail Requirements for Spectrometer Software**

<table>
<thead>
<tr>
<th>Requirement Number</th>
<th>Spectrometer Data System Feature Specification</th>
<th>Priority (M/D)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1.01</td>
<td>The system software requires an audit trail to monitor the creation, modification and deletion of all electronic records generated and managed by the system.</td>
<td>M</td>
</tr>
<tr>
<td>5.1.02</td>
<td>The audit trail covers all acquisition, control, calibration, calculation, display, reporting, and export functions and includes all file handling options such as open, copy, edit, rename, and delete.</td>
<td>M</td>
</tr>
<tr>
<td>5.1.03</td>
<td>The audit trail is able to support the system during normal operation without an excessive system overhead or loss of performance.</td>
<td>D</td>
</tr>
<tr>
<td>5.1.04</td>
<td>The audit trail once invoked cannot be switched off.</td>
<td>M</td>
</tr>
<tr>
<td>5.1.05</td>
<td>Archival of electronic records will have an audit trail entry.</td>
<td>M</td>
</tr>
<tr>
<td>5.1.06</td>
<td>Selected portions of the audit trail must be made available either by printing or viewing. These partial audit trail reports must be made available in a portable electronic format for use by regulatory agencies.</td>
<td>D</td>
</tr>
<tr>
<td>5.1.07</td>
<td>The audit trails must be maintained for as long as the electronic records they correspond to exist.</td>
<td>M</td>
</tr>
<tr>
<td>5.1.08</td>
<td>When a record is changed, all previous versions must be readable or available for inspection.</td>
<td>M</td>
</tr>
</tbody>
</table>

*Mandatory or desirable*
of the vendor) have been checked to ensure compliance with the regulations. The audit should be planned and should cover items such as the design and programming phases, product testing and release, documentation, and support; a report of the audit should be produced after the visit. Two published articles have covered vendor audits in more detail (3, 4).

The minimum audit is a remote vendor audit using a checklist that the vendor completes and returns to you. This is usually easy to complete, but the writer of the checklist must ensure that the questions are written in a way that can be understood by the recipient, because language and cultural issues could affect a remote checklist. Moreover, there is little way of checking the answers you receive. However, for smaller software systems — and some spectrometers fall into this category — a remote audit is a cost-effective way of getting information on how a vendor carries out its development process, so long as you know and understand its limitations.

**SYSTEM SELECTION: PART TWO**
If the vendor audit, price quote, instrument, and software are all acceptable, you'll be raising a capital expenditure request (or whatever it is called in your organization) and then generating a purchase order. The quote and the purchase order are a link in the validation chain; they provide a link into the next phase of the validation life cycle: qualification. The purchase order is the first stage in defining the initial configuration of the system, as we’ll discover in the next article in this series.

**REFERENCES**

**FOCUS ON QUALITY**

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.

**REFERENCES**

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

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

**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-

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

![Figure 2. A generic ion focusing system, showing position of ion optics relative to the interface cones and mass analyzer.](image)

![Figure 3. Extreme pressure drop in the ion optic chamber produces diffusion of electrons, resulting in a positively charged ion beam.](image)
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 4](image-url)  
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](image-url)  
Figure 5. Schematic of a multicomponent lens system with extraction lens and off-axis quadrupole mass analyzer (courtesy of Agilent Technologies [Wilmington, DE]).
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.

REFERENCES

(4) D. Potter, American Lab (July 1994).

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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 analyze 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 analyze ion 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...
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 $^{63}\text{Cu}$ 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 $^{63}\text{Cu}$ — 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 $^{63}\text{Cu}$. 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-

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

**Figure 3.** Profiles of different masses are built up using a multichannel data acquisition system.
ing power \((R)\), which in traditional mass spectrometry is represented by the following equation: \(R = \frac{m}{\Delta m}\), where \(m\) is the nominal mass at which the peak occurs and \(\Delta m\) 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.
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 — $^{63}\text{Cu}$ and $^{65}\text{Cu}$ — 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), the slight improvement has not become a practical benefit for most routine applications.

**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. 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. 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.

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 $1 \times 10^{-6}$ at $M – 1$ and $1 \times 10^{-7}$ 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 — $^{151}\text{Eu}^{++}$ 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 $^{151}\text{Eu}^{++}$, together with a scan of 1 ppb of As at mass 75. We can see very clearly that the $^{75}\text{As}$ signal lies on the sloping tail of the $^{151}\text{Eu}^{++}$ 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 QUADRUPOLE 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.

**REFERENCES**


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Although quadrupole mass analyzers represent more than 90% of all inductively coupled plasma mass spectrometry (ICP-MS) systems installed worldwide, limitations in their resolving power has led to the development of high-resolution spectrometers based on the double-focusing magnetic-sector design. Part VII of this series on ICP-MS takes a detailed look at this very powerful mass separation device, which has found its niche in solving challenging application problems that require excellent detection capability, exceptional resolving power, or very high precision.

As discussed in Part VI of this series (1), a quadrupole-based ICP-MS system typically offers a resolution of 0.7–1.0 amu. This is quite adequate for most routine applications, but has proved to be inadequate for many elements that are prone to argon-, solvent-, or sample-based spectral interferences. These limitations in quadrupoles drove researchers in the direction of traditional high-resolution, magnetic-sector technology to improve quantitation by resolving the analyte mass away from the spectral interference (2). These ICP-MS instruments, which were first commercialized in the late 1980s, offered resolving power as high as 10,000, compared with a quadrupole, which had a resolving power of approximately 300. This dramatic improvement in resolving power allowed difficult elements like Fe, K, As, V, and Cr to be determined with relative ease, even in complex sample matrices.

**TRADITIONAL MAGNETIC-SECTOR INSTRUMENTS**
The magnetic-sector design was first used in molecular spectroscopy for the structural analysis of complex organic compounds. Unfortunately, it was initially found to be unsuitable as a separation device for an ICP system because it required a few thousand volts of potential at the plasma interface area to accelerate the ions into the mass analyzer. For this reason, basic changes had to be made to the ion acceleration mechanism to optimize it as an ICP-MS separation device. This was a significant challenge when magnetic-sector systems were first developed in the late 1980s. However, by the early 1990s, instrument designers solved this problem by moving the high-voltage components away from the plasma and interface and closer to the mass spectrometer. Today’s instrumentation is based on two different approaches, commonly referred to as standard or reverse Nier-Johnson geometry. Both these designs, which use the same basic principles, consist of two analyzers — a traditional electromagnet and an electrostatic analyzer (ESA). In the standard (sometimes called forward) design, the ESA is positioned before the magnet, and in the reverse design it is positioned after the magnet. A schematic of a reverse Nier-Johnson spectrometer is shown in Figure 1.

**PRINCIPLES OF OPERATION**
With this approach, ions are sampled from the plasma in a conventional manner and then accelerated in the ion optic region to a few kilovolts before they enter the mass analyzer. The magnetic field, which is dispersive with respect to ion energy and mass, focuses all the ions into the mass analyzer. For this reason, basic changes had to be made to the ion acceleration mechanism to optimize it as an ICP-MS separation device. This was a significant challenge when magnetic-sector systems were first developed in the late 1980s. However, by the early 1990s, instrument designers solved this problem by moving the high-voltage components away from the plasma and interface and closer to the mass spectrometer. Today’s instrumentation is based on two different approaches, commonly referred to as standard or reverse Nier-Johnson geometry. Both these designs, which use the same basic principles, consist of two analyzers — a traditional electromagnet and an electrostatic analyzer (ESA). In the standard (sometimes called forward) design, the ESA is positioned before the magnet, and in the reverse design it is positioned after the magnet. A schematic of a reverse Nier-Johnson spectrometer is shown in Figure 1.
A plot of magnetic field strength, time was spent scanning and settling the magnet. This was not such a major problem for qualitative analysis, but proved to be impractical for routine trace element analysis. This concept is shown in greater detail in Figure 2, which is a plot of four parameters — magnetic field strength, accelerating voltage, mass, and signal intensity — against time for four separate masses \((M_1-M_4)\). Scanning the magnet from point \(A\) to point \(B\) (accelerating voltage is fixed) results in a scan across the mass range, generating spectral peaks for the four different masses. It can be seen that this increased scanning and settling overhead time (often referred to as dead time) would result in valuable measurement time being lost, particularly for high sample throughput that required ultra-trace detection levels.

Changing the electric field in the opposite direction to the field strength of the magnet during the cycle time of the magnet has the effect of “stopping” the mass that passes through the analyzer.

Because traditional magnetic-sector technology was initially developed for the structural or qualitative identification of organic compounds, there wasn’t a real necessity for rapid quantitation of spectral peaks required for trace element analysis. They functioned by scanning over a large mass range by varying the magnetic field over time with a fixed acceleration voltage. During a small window in time, which was dependent on the resolution chosen, ions of a particular mass-to-charge are swept past the exit slit to produce the characteristic flat top peaks. As the resolution of a magnetic-sector instrument is independent of mass, ion signals, particularly at low mass, are far apart. The result was that a large amount of time was spent scanning and settling the mass range, generating spectral peaks for trace element analysis. This concept is shown in greater detail in Figure 2, which is a plot of four parameters — magnetic field strength, accelerating voltage, mass, and signal intensity — against time for four separate masses \((M_1-M_4)\). Scanning the magnet from point \(A\) to point \(B\) (accelerating voltage is fixed) results in a scan across the mass range, generating spectral peaks for the four different masses. It can be seen that this increased scanning and settling overhead time (often referred to as dead time) would result in valuable measurement time being lost, particularly for high sample throughput that required ultra-trace detection levels.

Changing the electric field in the opposite direction to the field strength of the magnet during the cycle time of the magnet has the effect of “stopping” the mass that passes through the analyzer.

It should be pointed out that although this approach represents enormous time savings over older, single-focusing magnetic-sector technology, it is still significantly slower than quadrupole-based instruments. The inherent problem lies in the fact that a quadrupole can be electronically scanned much faster than a mass spectrometer.
magnet. Typical speeds for a full mass scan (0–250 amu) of a magnet are in the order of 400–500 ms, compared with 100 ms for a quadrupole. In addition, it takes much longer for magnets to slow down and settle to take measurements — typically 30–50 ms compared to 1–2 ms for a quadrupole. So, even though in practice, the electric scan dramatically reduces the overall analysis time, modern double-focusing magnetic-sector ICP-MS systems, especially when multiple resolution settings are used, are significantly slower than quadrupole instruments. This makes them less than ideal for routine, high-throughput applications or for samples that require multielement determinations on rapid transient signals.

**RESOLVING POWER**

As mentioned previously, most commercial magnetic-sector ICP-MS systems offer as much as 10,000 resolving power (5% peak height/10% valley definition), which is high enough to resolve the majority of spectral interferences. It’s worth emphasizing that resolving power (R) is represented by the equation: $R = \frac{m}{\Delta m}$, where m is the nominal mass at which the peak occurs and $\Delta m$ is the mass difference between two resolved peaks (6). In a quadrupole, the resolution is selected by changing the ratio of the rf/dc voltages on the quadrupole rods. However, because a double-focusing magnetic-sector instrument involves focusing ion angles and ion energies, mass resolution is achieved by using two mechanical slits — one at the entrance to the mass spectrometer and another at the exit, before the detector. Varying resolution is achieved by scanning the magnetic field under different entrance- and exit-slit width conditions. Similar to optical systems, low resolution is achieved by using wide slits, whereas high resolution is achieved with narrow slits. Varying the width of both the entrance and exit slits effectively changes the operating resolution. This can be seen in Figure 4, which shows two slit width scenarios. Figure 4a shows an example of a wide exit slit producing relatively low resolution and a characteristic flat-topped peak. Figure 4b shows the same size entrance slit, but a narrower exit slit, producing higher resolution with a characteristic triangular peak. The lowest practical resolution achievable with a double-focusing magnetic-sector instrument, using the widest entrance and exit slits, is approximately 300–400, whereas the highest practical resolution, using the narrowest entrance and exit slits, is approximately 10,000. Most commercial systems operate at fixed resolution settings — for example, low is typically 300–400; medium is typically 3000–4000, and high is typically 8000–10,000 (the choice of settings will vary depending on the instrumentation).

However, it should be emphasized that, similar to optical spectrometry, as the resolution is increased, the transmission decreases. So even though extremely high resolution is available, detection limits will be compromised under these conditions. This can be seen in Figure 5, which shows a plot of resolution against ion transmission. Figure 5 shows that a resolving power of 400 produces 100% transmission, but at a resolving power of 10,000, only ~2% is achievable. This dramatic loss in sensitivity could be an issue if low detection limits are required in spectrally complex samples that require the highest possible resolution; however, spectral demands of this nature are not very common. Table I shows the resolu-

**Table I.** Resolution required to resolve some common polyatomic interferences from a selected group of isotopes.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Matrix</th>
<th>Interference</th>
<th>Resolution</th>
<th>Transmission</th>
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<tr>
<td>$^{39}$K</td>
<td>$\text{H}_2\text{O}$</td>
<td>$^{38}\text{ArH}$</td>
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<td>6%</td>
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<tr>
<td>$^{40}$Ca</td>
<td>$\text{H}_2\text{O}$</td>
<td>$^{40}\text{Ar}$</td>
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<tr>
<td>$^{44}$Ca</td>
<td>$\text{HNO}_3$</td>
<td>$^{14}\text{N}^{14}\text{N}^{16}\text{O}$</td>
<td>970</td>
<td>80%</td>
</tr>
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<td>$^{56}$Fe</td>
<td>$\text{H}_2\text{O}$</td>
<td>$^{40}\text{Ar}^{16}\text{O}$</td>
<td>2504</td>
<td>18%</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>$\text{H}_2\text{O}$</td>
<td>$^{15}\text{N}^{16}\text{O}$</td>
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<td>53%</td>
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<td>$^{34}$S</td>
<td>$\text{H}_2\text{O}$</td>
<td>$^{16}\text{O}^{16}\text{O}$</td>
<td>1300</td>
<td>65%</td>
</tr>
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<td>$^{75}$As</td>
<td>$\text{HCl}$</td>
<td>$^{40}\text{Ar}^{35}\text{Cl}$</td>
<td>7725</td>
<td>2%</td>
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<td>$^{51}$V</td>
<td>$\text{HCl}$</td>
<td>$^{35}\text{Cl}^{16}\text{O}$</td>
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<tr>
<td>$^{64}$Zn</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$^{32}\text{S}^{16}\text{O}^{16}\text{O}$</td>
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<td>$^{52}$Cr</td>
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<td>$\text{HNO}_3$</td>
<td>$^{40}\text{Ar}^{15}\text{N}$</td>
<td>2300</td>
<td>20%</td>
</tr>
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</table>
tion required to resolve fairly common polyatomic interferences from a selected group of elemental isotopes, together with the achievable ion transmission.

Figure 6 is a comparison between a quadrupole instrument and a magnetic-sector instrument with one of the most common polyatomic interferences — $^{40}$Ar$^{16}$O on $^{56}$Fe, which requires a resolution of 2504 to separate the peaks. Figure 6a shows a spectral scan of $^{56}$Fe using a quadrupole instrument. What it doesn’t show is the massive polyatomic interference $^{40}$Ar$^{16}$O (produced by oxygen ions from the water combining with argon ions from the plasma) completely overlapping the $^{56}$Fe. It shows very clearly that these two masses are unresolvable with a quadrupole. If that same spectral scan is performed on a magnetic-sector instrument, the result is the scan shown in Figure 6b. To see the spectral scan on the same scale, it was necessary to examine a much smaller range. For this reason, a 0.100-amu window was taken, as indicated by the dotted lines.

OTHER BENEFITS

Besides high resolving power, another attractive feature of magnetic-sector instruments is their very high sensitivity combined with extremely low background levels. High ion transmission in low-resolution mode translates into sensitivity specifications of typically 100–200 million counts per second (mcps) per ppm, while background levels resulting from extremely low dark current noise are typically 0.1–0.2 cps. This compares with sensitivity of 10–50 mcps and background levels of ~10 cps for a quadrupole instrument. For this reason detection limits, especially for high-mass elements like uranium where high resolution is generally not required, are typically an order of magnitude better than those provided by a quadrupole-based instrument.

Besides good detection capability, another of the recognized benefits of the magnetic-sector approach is its ability to quantitate with excellent precision. Measurement of the characteristically flat-topped spectral peaks translates directly into high-precision data. As a result, in the low-resolution mode, relative standard deviation (RSD) values of 0.01–0.05% are fairly common, which makes magnetic-sector instruments an ideal tool for carrying out high-precision isotope ratio work (7). Although precision is usually degraded as resolution is increased (because the peak shape gets worse), modern instrumentation with high-speed electronics and low mass bias is still capable of precision values of <0.1% RSD in medium- or high-resolution mode (8).

The demand for ultrahigh-precision data, particularly in the field of geochemistry, has led to the development of instruments dedicated to isotope ratio analysis. These are based on the double-focusing magnetic-sector design, but instead of using just one detector, these instruments use multiple detectors. Often referred to as multicollector systems,
they offer the capability of detecting and measuring multiple ion signals at exactly the same time. As a result of this simultaneous measurement approach, they are recognized as producing the ultimate in isotope ratio precision (9).

There is no question that double-focusing magnetic-sector ICP-MS systems are no longer a novel analytical technique. They have proved themselves to be a valuable addition to the trace element toolkit, particularly for challenging applications that require good detection capability, exceptional resolving power, and very high precision. They do have their limitations, however, and perhaps should not be considered a competitor for quadrupole instruments when it comes to rapid, high-sample-throughput applications or when performing multielement determinations on fast transient peaks, using sampling accessories such as electrothermal vaporization (10) or laser ablation (11).

REFERENCES


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A Beginner’s Guide to ICP-MS
Part VIII — Mass Analyzers: Time-of-Flight Technology

Robert Thomas

Continuing with the discussion on mass analyzers used in inductively coupled plasma–mass spectrometry (ICP-MS), let’s now turn our attention to the most recent mass separation device to be commercialized — time-of-flight (TOF) technology. Although the first TOF mass spectrometer was first described in the literature in the late 1940s (1), it has taken more than 50 years to adapt it for use in an ICP-MS system. The recent growth in TOF ICP-MS sales is in response to the technology’s unique ability to sample all ions generated in the plasma at exactly the same time, which is advantageous in three major areas:

- Multielement determinations of rapid transient signals generated by sampling accessories such as laser ablation and electrothermal vaporization devices
- High-precision, ratioing techniques such as internal standardization and isotope ratio analysis
- Rapid multielement measurements, especially where sample volume is limited.

TOF’s simultaneous nature of sampling ions offers distinct advantages over traditional scanning (sequential) quadrupole technology for ICP-MS applications where large amounts of data need to be captured in a short amount of time. Before we go on to discuss this in greater detail, let’s go through the basic principles of TOF analyzers.

**BASIC PRINCIPLES OF TOF**

All TOF-MS instruments are based on the same fundamental principle that the kinetic energy ($E_k$) of an ion is directly proportional to its mass ($m$) and velocity ($v$), represented by equation 1

$$E_k = \frac{1}{2}mv^2 \quad [1]$$

Therefore, if a population of ions — all having different masses — are given the same kinetic energy by an accelerating voltage ($U$), the velocities of the ions will all be different, based on their masses. This principle is then used to separate ions of different mass-to-charge ratios ($m/z$) in the time ($t$) domain, over a fixed flight path distance ($D$) — represented by equation 2

$$m/z = 2U^2/D^2 \quad [2]$$

This is shown schematically in Figure 1, with three ions of different mass-to-charge ratios being accelerated into a flight tube and arriving at the detector at different times. It can be seen that, based on their velocities, the lightest ion arrives first, followed by the medium mass ion, and finally the heaviest one. Using flight tubes of 1 m in length, even the heaviest ions typically take less than 50 μs to reach the detector. This translates into approximately 20,000 mass spectra/s — approximately 2–3 orders of magnitude faster than the sequential scanning mode of a quadrupole system.

**DIFFERENT SAMPLING APPROACHES**

Even though this process sounds fairly straightforward, sampling the ions in a simultaneous manner from a continuous source of ions being generated in the plasma discharge is not a trivial task. Basically two sampling approaches are used in commercial TOF mass analyzers. They are the orthogonal design (2), where the flight tube is positioned at right angles to the sampled ion beam, and the axial design (3), where the flight tube is in the same axis as the ion beam. In both designs, all ions that contribute to the mass spectrum are sampled through the interface cones, but instead of being focused into the mass filter in the conventional way, packets (groups) of ions are electrostatically injected into the flight tube at exactly the same time. With the orthogonal approach, an accelerating potential is applied at right angles to the continuous ion beam from the plasma source. The ion beam is then chopped by using a pulsed voltage supply coupled to the orthogonal accelerator to provide repetitive voltage slices at a frequency of a few kilohertz. The sliced packets of ions, which are typically long and thin in cross section (in the vertical plane), are then allowed to drift into the flight tube where the ions are temporally resolved according to their velocities. Figure 2 shows this process schematically.

With the axial approach, an accelerating potential is applied axially (in the same axis) to the incoming ion beam as it enters the extraction region. Because the ions are in the same plane as the detector, the beam has to be modulated using an electrode grid to repel the gated packet of ions into the flight tube. This kind of modulation generates an ion packet that is long and thin in cross section (in the horizontal plane). The differ-

![Figure 1. Principles of ion detection using TOF technology, showing separation of three masses in the time domain.](image-url)
ent masses are then resolved in the time
domain in a similar manner to the orthog-
onal design. The layout of an on-axis
TOF system is shown schematically in
Figure 3.

Figures 2 and 3 represent a rather sim-
plistic explanation of TOF principles of
operation. In practice, the many complex
ion focusing components in a TOF mass
analyzer ensure that a maximum number
of analyte ions reach the detector and
also that undesired photons, neutral
species, and interferences are ejected
from the ion beam. Some of these compo-

nents are shown in Figure 4, which
shows a more detailed view of a typical
orthogonal system. This design shows
that an injector plate is used to inject
packets of ions at right angles from the
ion beam emerging from the MS inter-
face. These packets of ions are then di-
rected toward a deflection–steering plate
where pulsed voltages steer the ions (or
throw out unwanted species) in the direc-
tion of a reflectron. The packets of ions
are then deflected back 180º, where they
are detected by a channel electron multi-
plier or discrete dynode detector. The
reflectron is a type of ion mirror and func-
tions as an energy compensation device,
so that different ions of the same mass ar-
rive at the detector at the same time.

Even though the on-axis design might
use slightly different components, the
principles are very similar.

DIFFERENCES BETWEEN ORTHOGONAL
AND ON-AXIS TOF TECHNOLOGY

Although there are real benefits of using
TOF over quadrupole technology for
some ICP-MS applications, each type of
TOF design also has subtle differences in
its capabilities. (However, it is not the in-
tent of this tutorial to make any personal
judgement about the benefits or disad-
vantages of either design.) Let’s take a
look at some of these differences in
greater detail (4, 5).

Sensitivity. The axial approach tends to
produce higher ion transmission because
the steering components are in the same
plane as the ion generation system
(plasma) and the detector. This means
that the direction and magnitude of great-
est energy dispersion is along the axis of
the flight tube. In addition, when ions are
extracted orthogonally, the energy dis-
\n
persion can produce angular divergence
of the ion beam resulting in poor trans-
mission efficiency. However, the sensitiv-
ity of either TOF design is still generally

lower than the latest commercial quadru-
pole instruments.

Background levels. The on-axis design
tends to generate higher background lev-
els because neutral species and photons
stand a greater chance of reaching the
detector. This results in background lev-
els in the order of 20–50 counts/s —
approximately 5–10 times higher than the
orthogonal design. However, because the
ion beam in the axial design has a smaller
cross section, a smaller detector can be
used, which generally has better noise
characteristics. In comparison, most com-
mercial quadrupole instruments offer
background levels of 1–10 counts/s,
depending on the design.

Duty cycle. Duty cycle is usually defined
as the fraction (percentage) of extracted
ions that actually make it into the mass
analyzer. Unfortunately, with a TOF ICP-
MS system that has to use pulsed ion
packets from a continuous source of ions
generated in the plasma, this process is
not very efficient. It should be empha-
sized that even though the ions are sam-
ped at the same time, detection is not si-
ultaneous because different masses
arrive at the detector at different times.
The difference between the sampling
mechanisms of orthogonal and axial TOF
designs translates into subtle differences
in their duty cycles.
With the orthogonal design, duty cycle is defined by the width of the extracted ion packets, which are typically long and thin in cross section, as shown in Figure 2. In comparison, the duty cycle of the axial design is defined by the length of the extracted ion packets, which are typically wide and thin in cross section, as shown in Figure 3. Duty cycle can be improved by changing the cross-sectional area of the ion packet but, depending on the design, is generally improved at the expense of resolution. In practice, the duty cycles for both orthogonal and axial designs are in the order of 15–20%.

**Resolution.** The resolution of the orthogonal approach is slightly better because of its two-stage extraction/acceleration mechanism. Because a pulse of voltage pushes the ions from the extraction area into the acceleration region, the major energy dispersion lies along the axis of ion generation. For this reason, the energy spread is relatively small in the direction of extraction compared to the axial approach, resulting in better resolution. However, the resolving power of both commercial TOF ICP-MS systems is typically in the order of 500–2000 (4), depending on the mass region, which makes them inadequate to resolve many of the problematic polyatomic species encountered in ICP-MS (6). In comparison, commercial high-resolution systems based on the double-focusing magnetic-sector design offer resolving power as high as 10,000, while commercial quadrupoles typically achieve 300–400.

**Mass bias.** This is the degree to which ion transport efficiency varies with mass. All instruments show some degree of mass bias, which is usually compensated for by measuring the difference between the theoretical and observed ratio of two isotopes of the same element. In TOF, the velocity (energy) of the initial ion beam will affect the instrument’s mass bias characteristics. In theory, mass bias should be less with the axial design because the extracted ion packets don’t have any velocity in a direction perpendicular to the axis of the flight tube, which could potentially impact their transport efficiency.

**BENEFITS OF TOF TECHNOLOGY FOR ICP-MS**

It should be emphasized that these performance differences between the two designs are subtle and should not detract from the overall benefits of the TOF approach for ICP-MS. As mentioned earlier, a scanning device such as a quadrupole can only detect one mass at a time, which means that a compromise always exists between number of elements, detection limits, precision, and the overall measurement time. However, with the TOF approach, the ions are sampled at exactly the same moment in time, which means that multielement data can be collected with no significant deterioration in quality. The ability of a TOF system to capture a full mass spectrum, significantly faster than a quadrupole, translates into three major benefits.

**RAPID TRANSIENT PEAK ANALYSIS**

Probably the most exciting potential for TOF ICP-MS is in the multielement analysis of a rapid transient signal generated by sampling accessories such as laser ablation (7), electrothermal vaporization, and flow injection systems (4). Even though a scanning quadrupole can be used for this type of analysis, it struggles...
to produce high-quality, multielement data when the transient peak lasts only a few seconds. The simultaneous nature of TOF instrumentation makes it ideally suited for this type of analysis, because the entire mass range can be collected in less than 50 μs. Figure 5 shows a full mass scan of a transient peak generated by an electrothermal vaporization sampling accessory coupled to a TOF ICP-MS system. The technique has generated a healthy signal for 10 μL of a 5-ppb multielement solution in less than 10 s. TOF technology is probably better suited than any other design of ICP-MS for this type of application.

**IMPROVED PRECISION**

To better understand how TOF technology can help improve precision in ICP-MS, it is important to know the major sources of instability. The most common source of noise in ICP-MS is flicker noise associated with the sample introduction process (from peristaltic pump pulsations, nebulization mechanisms, and plasma fluctuations) and shot noise derived from photons, electrons, and ions hitting the detector. Shot noise is based on counting statistics and is directly proportional to the square root of the signal. It therefore follows that as the signal intensity gets larger, the shot noise has less of an impact on the precision (% RSD) of the signal. At high ion counts the most dominant source of imprecision in ICP-MS is derived from flicker noise generated in the sample introduction area.

One of the most effective ways to reduce instability produced by flicker noise is to use a technique called internal standardization, where the analyte signal is compared and ratioed to the signal of an internal standard element (usually of similar mass and ionization characteristics) that is spiked into the sample. Even though a quadrupole-based system can do an adequate job of compensating for these signal fluctuations, it is ultimately limited by its inability to measure the internal standard at exactly the same time as the analyte isotope. So to compensate...
for sample introduction— and plasma-based noise and achieve high precision, the analyte and internal standard isotopes need to be sampled and measured simultaneously. For this reason, the design of a TOF mass analyzer is perfect for true simultaneous internal standardization required for high-precision work. It follows, therefore, that TOF is also well suited for high-precision isotope ratio analysis where its simultaneous nature of measurement is capable of achieving precision values close to the theoretical limits of counting statistics. And unlike a scanning quadrupole-based system, it can measure ratios for as many isotopes or isotopic pairs as needed—all with excellent precision (8).

ANALYSIS TIME
As with a scanning ICP–optical emission spectroscopy system, the speed of a quadrupole ICP mass spectrometer is limited by its scanning rate. To determine 10 elements in duplicate with good precision and detection limits, an integration time of 3 s/mass is normally required. When overhead scanning and settling times are added for each mass and each replicate, this translates to approximately 2 min/sample. With a TOF system, the same analysis would take significantly less time because all the data are captured simultaneously. In fact, detection limit levels in a TOF instrument are typically achieved using a 10–30 s integration time, which translates into a 5–10-fold improvement in measurement time over a quadrupole instrument. The added benefit of a TOF instrument is that the speed of analysis is not impacted by the number of analytes being determined. It wouldn’t matter if the suite of elements in the method was 10 or 70 — the measurement time would be approximately the same. However, one point must be stressed: A large portion of the overall analysis time is taken up with flushing an old sample out and pumping a new sample into the sample introduction system. This can be as much as 2 min/sample for real-world matrices. So when this time is taken into account, the difference between the sample throughput of a quadrupole system and a TOF ICP-MS system is not so evident.

TOF ICP-MS, with its rapid, simultaneous mode of measurement, excels at multielement applications that generate fast transient signals. It offers excellent precision, particularly for isotope-ratioing techniques, and also has the capability for high speeds of analysis. However, even though it has enormous potential, TOF was only commercialized in 1998, so it is relatively immature compared with quadrupole ICP-MS technology, which is almost 20 years old. For that reason, there is currently only a small number of TOF instruments carrying out high-throughput, routine applications.

REFERENCES

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A Beginner’s Guide to ICP-MS
Part IX — Mass Analyzers: Collision/Reaction Cell Technology

Robert Thomas

The detection capability of traditional quadrupole mass analyzers for some critical elements is severely compromised by the formation of polyatomic spectral interferences generated by either argon, solvent, or sample-based ionic species. Although there are ways to minimize these interferences — including correction equations, cool plasma technology, and matrix separation — they cannot be completely eliminated. However, a new approach called collision/reaction cell technology has recently been developed that virtually stops the formation of many of these harmful species before they enter the mass analyzer. Part IX of this series takes a detailed look at this innovative new technique and the exciting potential it has to offer.

A small number of elements are recognized as having poor detection limits by inductively coupled plasma mass spectrometry (ICP-MS). These elements are predominantly ones that suffer from major spectral interferences generated by ions derived from the plasma gas, matrix components, or the solvent–acid used to get the sample into solution. Examples of these interferences include:
- \(^{38}\text{ArH}\) on the determination of \(^{39}\text{K}\)
- \(^{40}\text{Ar}\) on the determination of \(^{40}\text{Ca}\)
- \(^{40}\text{Ar}^{16}\text{O}\) on the determination of \(^{80}\text{Se}\)
- \(^{35}\text{Cl}^{16}\text{O}\) on the determination of \(^{51}\text{V}\).

The cold/cool plasma approach, which uses a lower temperature to reduce the formation of the argon-based interferences, is a very effective way to get around some of these problems (1); however, it is sometimes difficult to optimize, it is only suitable for a few of the interferences, it is susceptible to more severe matrix effects, and it can be time consuming to change back and forth between normal- and cool-plasma conditions. These limitations and the desire to improve performance led to the development of collision/reaction cells in the late 1990s. Designed originally for organic MS to generate daughter species to confirm the structure of the parent molecule (2), they were used in ICP-MS to stop the appearance of many argon-based spectral interferences.

Basic Principles of Collision/Reaction Cells
With this approach, ions enter the interface in the normal manner, where they are extracted under vacuum into a collision/reaction cell that is positioned before the analyzer quadrupole. A collision/reaction gas such as hydrogen or helium is then bled into the cell, which consists of a multipole (a quadrupole, hexapole, or octapole), usually operated in the radio frequency (rf)-only mode. The rf-only field does not separate the masses like a traditional quadrupole, but instead has the effect of focusing the ions, which then collide and react with molecules of the collision/reaction gas. By a number of different ion-molecule collision and reaction mechanisms, polyatomic interfering ions like \(^{40}\text{Ar}\), \(^{40}\text{Ar}^{16}\text{O}\), and \(^{38}\text{ArH}\), will either be converted to harmless noninterfering species, or the analyte will be converted to another ion which is not interfered with. This is exemplified by the reaction [1], which shows the use of hydrogen gas to reduce the \(^{38}\text{ArH}\) polyatomic interference in the determination of \(^{39}\text{K}\).

Hydrogen gas converts \(^{38}\text{ArH}\) to the harmless \(^{3}H^{1}\) ion and atomic argon, but does not react with the potassium. The \(^{39}\text{K}\) analyte ions, free of the interference, then emerge from the collision/reaction cell, where they are directed toward the quadrupole analyzer for normal mass separation.
Discrimination by Kinetic Energy
The first commercial collision cells for ICP-MS were based on hexapole technology (3), which was originally designed for the study of organic molecules using tandem MS. The more collision-induced daughter species that were generated, the better the chance of identifying the structure of the parent molecule; however, this very desirable characteristic for liquid chromatography or electrospray MS studies was a disadvantage in inorganic MS, where secondary reaction-product ions are something to be avoided. There were ways to minimize this problem, but they were still limited by the type of collision gas that could be used. Unfortunately, highly reactive gases — such as ammonia and methane, which are more efficient at interference reduction — could not be used because of the limitations of a non-scan-ning hexapole (in rf-only mode) to adequately control the secondary reactions. The fundamental reason is that hexapoles do not provide adequate mass discrimination capabilities to suppress the unwanted secondary reactions, which necessitates the need for kinetic energy discrimination to distinguish the collision product ions from the analyte ions. This is typically achieved by setting the collision cell bias slightly less positive than the mass filter bias. This means that the collision-product ions, which have the same energy as the cell bias, are discriminated against and rejected, while the analyte ions, which have a higher energy than the cell bias, are transmitted.

The inability to adequately control the secondary reactions meant that low reactivity gases like He, H₂, and Xe were the only option. The result was that ion-molecule collisional fragmentation (and not reactions) was thought to be the dominant mechanism of interference reduction. So even though the ion transmission characteristics of a hexapole were considered very good (with respect to the range of energies and masses transmitted), background levels were still relatively high because the interference rejection process was not very efficient. For this reason, its detection capability — particularly for some of the more difficult elements, like Fe, K, and Ca — offered little improvement over the cool plasma approach. Table I shows some typical detection limits in ppb achievable with a hexapole-based collision cell ICP-MS system (4).

Recent modifications to the hexapole design have significantly improved its

![Figure 1. Layout of a typical collision/reaction cell instrument.](image)

**Table I. Typical detection limits (in ppb) achievable with a hexapole-based collision cell ICP-MS system (4).**

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Elemental Sensitivity (cps/µg/mL)</th>
<th>Detection Limit (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>9</td>
<td>6.9 x 10⁴</td>
<td>0.0077</td>
</tr>
<tr>
<td>Mg</td>
<td>24</td>
<td>1.3 x 10⁴</td>
<td>0.028</td>
</tr>
<tr>
<td>Ca</td>
<td>40</td>
<td>2.8 x 10⁴</td>
<td>0.07</td>
</tr>
<tr>
<td>V</td>
<td>51</td>
<td>1.7 x 10⁴</td>
<td>0.0009</td>
</tr>
<tr>
<td>Cr</td>
<td>52</td>
<td>2.4 x 10⁴</td>
<td>0.0007</td>
</tr>
<tr>
<td>Mn</td>
<td>55</td>
<td>3.4 x 10⁴</td>
<td>0.0017</td>
</tr>
<tr>
<td>Fe</td>
<td>56</td>
<td>3.0 x 10⁴</td>
<td>0.0017</td>
</tr>
<tr>
<td>Co</td>
<td>59</td>
<td>2.7 x 10⁴</td>
<td>0.0007</td>
</tr>
<tr>
<td>Ni</td>
<td>60</td>
<td>2.1 x 10⁴</td>
<td>0.016</td>
</tr>
<tr>
<td>Cu</td>
<td>63</td>
<td>1.9 x 10⁴</td>
<td>0.003</td>
</tr>
<tr>
<td>Zn</td>
<td>68</td>
<td>1.1 x 10⁴</td>
<td>0.008</td>
</tr>
<tr>
<td>Sr</td>
<td>88</td>
<td>4.9 x 10⁴</td>
<td>0.0003</td>
</tr>
<tr>
<td>Ag</td>
<td>107</td>
<td>3.5 x 10⁴</td>
<td>0.0003</td>
</tr>
<tr>
<td>Cd</td>
<td>114</td>
<td>2.4 x 10⁴</td>
<td>0.0004</td>
</tr>
<tr>
<td>Te</td>
<td>128</td>
<td>1.3 x 10⁴</td>
<td>0.009</td>
</tr>
<tr>
<td>Ba</td>
<td>138</td>
<td>5.9 x 10⁴</td>
<td>0.0002</td>
</tr>
<tr>
<td>Tl</td>
<td>205</td>
<td>4.0 x 10⁴</td>
<td>0.0002</td>
</tr>
<tr>
<td>Pb</td>
<td>208</td>
<td>3.7 x 10⁴</td>
<td>0.0007</td>
</tr>
<tr>
<td>Bi</td>
<td>209</td>
<td>3.4 x 10⁴</td>
<td>0.0005</td>
</tr>
<tr>
<td>U</td>
<td>238</td>
<td>2.3 x 10⁴</td>
<td>0.0001</td>
</tr>
</tbody>
</table>
collision/reaction characteristics. In addition to offering good transmission characteristics and kinetic energy discrimination, they now appear to offer basic mass-dependent discrimination capabilities. This means that the kinetic energy discrimination barrier can be adjusted with analytical mass, which offers the capability of using small amounts of highly reactive gases. Figure 2 shows an example of the reduction of both $^{40}$Ar$^{12}$C and $^{37}$Cl$^{16}$O using helium with a small amount of ammonia, in the isotopic ratio determination of $^{52}$Cr/$^{53}$Cr (52Cr is 83.789% and 53Cr is 9.401% abundant). It can be seen that the $^{52}$Cr/$^{53}$Cr ratio is virtually the same in the chloride and carbon matrices as it is with no matrix present when the optimum flow of collision/reaction gas is used (5).

Another way to discriminate by kinetic energy is to use an octapole in the collision/reaction cell instead of a hexapole. The benefit of using a higher order design is that its transmission characteristics, particularly at the low mass end, are slightly higher than lower order multipoles. Similar in design to the hexapole, collisional fragmentation and energy discrimination are the predominant mechanisms for interference reduction, which means that lower reactivity gases like hydrogen and helium are preferred. By careful design of the interface and the entrance to the cell, the collision/reaction capabilities can be improved, by reducing the number of sample/solvent/plasma-based ions entering the cell. This enables the collision gas to be more effective at reducing the interferences. An example of this is the use of H$_2$ as the cell gas to reduce the argon dimer ($^{40}$Ar$_2$) interference in the determination of the major isotope of selenium at mass 80 ($^{79}$Se). Figure 3 shows an example of a dramatic reduction in the $^{40}$Ar$_2$ background at mass 80 using an ICP-MS fitted with an octapole reaction cell. By using the optimum flow of H$_2$, the spectral background is reduced by about six orders of magnitude, from 10,000,000 cps to 10 cps, producing a background equivalent concentration of approximately 1 ppt for $^{79}$Se (6).

**Discrimination by Mass**

The other way to reject the products of the secondary reactions/collisions is to discriminate them by mass. Unfortunately, higher order multipoles cannot be used for efficient mass discrimination because the stability boundaries are diffuse, and sequential secondary
reactions cannot be easily intercepted. The way around this problem is to use a quadrupole (instead of a hexapole or octapole) inside the reaction/collision cell, and use it as a selective bandpass filter. The benefit of this approach is that highly reactive gases can be used, which tend to be more efficient at interference reduction. One such development that uses this approach is called dynamic reaction cell technology (7, 8). Similar in appearance to the hexapole and octapole collision/reaction cells, the dynamic reaction cell is a pressurized multipole positioned before the analyzer quadrupole. However, the similarity ends there. In dynamic reaction cell technology, a quadrupole is used instead of a hexapole or octapole. A highly reactive gas, such as ammonia or methane, is bled into the cell, which is a catalyst for ion molecule chemistry to take place. By a number of different reaction mechanisms, the gaseous molecules react with the interfering ions to convert them either into an innocuous species different from the analyte mass or a harmless neutral species. The analyte mass then emerges from the dynamic reaction cell free of its interference and steered into the analyzer quadrupole for conventional mass separation. The advantages of using a quadrupole in the reaction cell is that the stability regions are much better defined than a hexapole or octapole, so it is relatively straightforward to operate the quadrupole inside the reaction cell as a mass or bandpass filter, and not just an ion-focusing guide. Therefore, by careful optimization of the quadrupole electrical fields, unwanted reactions between the gas and the sample matrix or solvent (which could potentially lead to new interferences) are prevented. Therefore, every time an analyte and interfering ions enter the dynamic reaction cell, the bandpass of the quadrupole can be optimized for that specific problem and then changed on-the-fly for the next one. Figure 4 shows a schematic of an analyte ion $^{56}$Fe and an isobaric interference $^{40}$Ar$^{16}$O entering the dynamic reaction cell. The reaction gas NH$_3$ reacts with the ArO$^+$ to form atomic oxygen and argon together with a positive NH$_3$ ion. The quadrupole’s electrical field is then set to allow the transmission of the analyte ion $^{56}$Fe to the analyzer quadrupole, free of the problematic isobaric interference, $^{40}$Ar$^{16}$O. In addition, the NH$_3$ is prevented from reacting further to produce a new interfering ion. The advantage of this approach is that highly reactive gases can be used, which increases the number of ion–molecule reactions taking place and therefore more efficient removal of the interfering species. Of course, this also potentially generates more side reactions between the gas and the sample matrix and solvent; however, by dynamically scanning the bandpass of the quadrupole in the reaction cell, these reaction by-products are rejected before they can react to form new interfering ions.

**Collision/reaction cells have given a new lease on life to quadrupole mass analyzers used in ICP-MS.**

Table II. Typical detection limits in ppt of an ICP-MS system fitted with a dynamic reaction cell (9).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Detection Limit (ppt)</th>
<th>Analyte</th>
<th>Detection Limit (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.08</td>
<td>Co</td>
<td>0.07</td>
</tr>
<tr>
<td>Be</td>
<td>0.6</td>
<td>$^{40}$Ni</td>
<td>0.4</td>
</tr>
<tr>
<td>B</td>
<td>1.1</td>
<td>Zn</td>
<td>1</td>
</tr>
<tr>
<td>Na</td>
<td>0.3</td>
<td>As</td>
<td>1.2</td>
</tr>
<tr>
<td>Mg</td>
<td>0.6</td>
<td>Se*</td>
<td>5</td>
</tr>
<tr>
<td>Al</td>
<td>0.07</td>
<td>Sr</td>
<td>0.02</td>
</tr>
<tr>
<td>K*</td>
<td>1</td>
<td>Rh</td>
<td>0.01</td>
</tr>
<tr>
<td>$^{40}$Ca*</td>
<td>1</td>
<td>In</td>
<td>0.01</td>
</tr>
<tr>
<td>V*</td>
<td>0.3</td>
<td>Sb</td>
<td>0.06</td>
</tr>
<tr>
<td>Cr*</td>
<td>0.25</td>
<td>Cs</td>
<td>0.03</td>
</tr>
<tr>
<td>Mn*</td>
<td>0.09</td>
<td>Pb</td>
<td>0.03</td>
</tr>
<tr>
<td>$^{56}$Fe*</td>
<td>0.15</td>
<td>U</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* Indicates elements determined in dynamic reaction cell mode.
NH₃ gas and the ⁴⁰Ar interference, which is predominantly a charge exchange, occurs because the ionization potential of NH₃ (10.2 eV) is low compared with that of Ar (15.8 eV). Therefore, the reaction is exothermic and fast; however, the ionization potential of Ca (6.1 eV) is significantly less than that of NH₃, so the reaction, which is endothermic, is not allowed to proceed (8). Figure 5 shows this process in greater detail.

This highly efficient reaction mechanism translates into a dramatic reduction of the spectral background at mass 40, which is shown graphically in Figure 6. At the optimum NH₃ flow, a reduction in the ⁴⁰Ar background signal of about eight orders of magnitude is achieved, resulting in a detection limit of 0.5–1.0 ppt for ⁴⁰Ca.

Table II shows some typical detection limits in parts per trillion (ppt) of an ICP-MS system fitted with a dynamic reaction cell. The elements with an asterisk were determined using ammonia or methane as the reaction gas, while the other elements were determined in the standard mode (no reaction gas).

Collision/reaction cells have given a new lease on life to quadrupole mass analyzers used in ICP-MS. They have enhanced its performance and flexibility, and most definitely opened up the technique to more-demanding applications that were previously beyond its capabilities. However, it must be emphasized that even though differences exist between commercially available instruments, they all perform very well. The intent of this tutorial is to present the benefits of the technology to beginners and give an overview of the different approaches available. If it has created an interest, I strongly suggest that a performance evaluation is made based on your own sample matrices.

References
A Beginner’s Guide to ICP-MS
Part X — Detectors
Robert Thomas

Part X of this series on ICP-MS discusses the detection system — an important area of the mass spectrometer that counts the number of ions emerging from the mass analyzer. The detector converts the ions into electrical pulses, which are then counted by its integrated measurement circuitry. The magnitude of the electrical pulses corresponds to the number of analyte ions present in the sample. Trace element quantitation in an unknown sample is then carried out by comparing the ion signal with known calibration or reference standards.

Since inductively coupled plasma–mass spectrometry (ICP-MS) was first introduced in the early 1980s, a number of different ion detection designs have been used, the most popular being electron multipliers for low ion-count rates, and Faraday collectors for high-count rates. Today, the majority of ICP-MS systems used for ultratrace analysis use detectors that are based on the active film or discrete dynode electron multiplier. They are very sophisticated pieces of equipment compared with earlier designs and are very efficient at converting ion currents into electrical signals. Before we describe these detectors in greater detail, it is worth looking at two of the earlier designs — the channel electron multiplier (channeltron) and the Faraday collector — to get a basic understanding of how the ICP-MS ion detection process works.

**Channel electron multiplier.** The operating principles of the channel electron multiplier are similar to those of a photomultiplier tube used in ICP–optical emission spectroscopy (ICP-OES); however, instead of using individual dynodes to convert photons to electrons, the channeltron is an open glass cone — coated with a semiconductor-type material — that generates electrons from ions impinging on its surface. For the detection of positive ions, the front of the cone is biased at a negative potential and the far end, nearest the collector, is kept at ground. When the ion emerges from the quadrupole mass analyzer, it is attracted to the high negative potential of the cone. When the ion hits this surface, one or more secondary electrons form. The potential gradient inside the tube varies based on position, so the secondary electrons move farther down the tube. As these electrons strike new areas of the coating, more secondary electrons are emitted. This process is repeated many times. The result is a discrete pulse that contains many millions of electrons generated from an ion that first hits the cone of the detector (1). This process is shown simplistically in Figure 1.

This pulse is then sensed and detected by a very fast preamplifier. The output pulse from the preamplifier then goes to a digital discriminator and counting circuitry, which counts only pulses above a certain threshold value. This threshold level needs to be high enough to discriminate against pulses caused by spurious emission inside the tube, stray photons from the plasma itself, or photons generated from fast moving ions striking the quadrupole rods.

For some applications where ultratrace detection limits are not required, the ion beam from the mass analyzer is directed into a simple metal electrode, or Faraday cup.

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These Figure 1. The path of an ion through a channel electron multiplier.

ner. This situation is caused by ions arriving at the detector during the output pulse of the preceding ion and not being detected by the counting system. This “dead time,” as it is known, is a fundamental limitation of the multiplier detector and is typically 30–50 ns, depending on the detection system. Compensation in the measurement circuitry has to be made for this dead time in order to count the maximum number of ions hitting the detector.

**Faraday cup.** For some applications where ultratrace detection limits are not required, the ion beam from the mass analyzer is directed into a simple metal electrode, or Faraday cup (1). With this approach, there is no control over the applied voltage (gain), so a Faraday cup can only be used for high ion currents. Their lower working range is in the order of 10⁴ counts/s, which means that if a Faraday cup is to be used as the only detector, the sensitivity of the ICP mass spectrometer will be severely compromised. For this reason, Faraday cups are normally used in conjunction with a channeltron or discrete dynode detector to extend the dynamic range of the instrument. An additional problem with the Faraday cup is that, because of the time constant used in the dc amplification process to measure the ion current, it is limited to relatively low scan rates. This limitation makes it unsuitable for the rapid scan rates required for traditional pulse counting used in ICP-MS and also limits its ability to handle fast transient peaks.

The Faraday cup never became popular with quadrupole ICP-MS systems because it wasn’t suitable for very low ion-count rates. An attempt was made in the early 1990s to develop an ICP-MS system using a Faraday cup detector for environmental applications, but its sensitivity was compromised and, as a result, it was considered more suitable for applications requiring ICP-OES detection capability. However, Faraday cup technology is still used in some magnetic sector instruments, particularly where high ion signals are encountered in the determination of way the measurement circuitry handles low and high ion-count rates. When ICP-MS was first commercialized, it could only handle as many as five orders of dynamic range; however, when attempts were made to extend the dynamic range, certain problems were encountered. Before we discuss how modern detectors deal with this issue, let’s first take a look at how it was addressed in earlier instrumentation.

**When ICP-MS was first commercialized, it could only handle as many as five orders of dynamic range; when attempts were made to extend the dynamic range, certain problems were encountered.**

**Extending the Dynamic Range**

Traditionally, ICP-MS using the pulse counting measurement is capable of about five orders of linear dynamic range. This means that ICP-MS calibration curves, generally speaking, are linear from ppt levels to as much as a few hundred parts-per-billion. However, a number of ways exist to extend the dynamic range of ICP-MS another three to four orders of magnitude to work from sub-part-per-trillion levels, to as much as 100 ppm. Following is a brief overview of some of the different approaches that have been used.

**Filtering the ion beam.** One of the first approaches to extend the dynamic range in ICP-MS was to filter the ion beam by putting a non-optimum voltage on one of the ion lens components or the quadrupole itself to limit the number of ions reaching the detector. This voltage offset, which was set on an individual mass basis, acted as an energy filter to electronically screen the ion beam and reduce the subsequent ion signal to within a range covered by pulse-counting ion detection. The main disadvantage with this approach was that the operator had to have prior knowledge of the sample to know what voltage to apply to the high concentration masses.
**Tutorial**

**Using two detectors.** Another technique that was implemented in some of the early quadrupole ICP-MS instrumentation was to use two different detectors, such as a channel electron multiplier to measure low current signals, and a Faraday cup to measure high ion currents. This process worked reasonably well, but struggled with some applications because it required rapid switching between the two detectors. The problem was that the ion beam had to be physically deflected to select the optimum detector. Not only did this degrade the measurement duty cycle, but detector switching and stabilization times of several seconds also precluded fast transient signal detection.

The more modern approach is to use just one detector to extend the dynamic range. By using the detector in both the pulse-counting and analog modes, high and low concentrations can be determined in the same sample. Three approaches use this type of detection system; two of them involve carrying out two scans of the sample, while the third uses only one scan.

**Using two scans with one detector.** The first approach uses an electron multiplier operated in both digital and analog modes (3). Digital counting provides the highest sensitivity, while operation in the analog mode (achieved by reducing the high voltage applied to the detector) is used to reduce the sensitivity of the detector, thus extending the concentration range for which ion signals can be measured. The system is implemented by scanning the spectrometer twice for each sample. A first scan, in which the detector is operated in the analog mode, provides signals for elements present at high concentrations. A second scan, in which the detector voltage is switched to digital-pulse counting mode, provides high sensitivity detection for elements present at low levels. A major advantage of this technology is that users do not need to know in advance whether to use analog or digital detection because the system automatically scans all elements in both modes. However, its disadvantage is that two independent mass scans are required to gather data across an extended signal range. This not only results in degraded measurement efficiency and slower analyses, but it also means that the system cannot be used for fast transient signal analysis of unknown samples because mode switching is generally too slow.

The second way of extending the dynamic range is similar to the first approach, except that the first scan is used as an investigative tool to examine the sample spectrum before analysis (4). This first prescan establishes the mass positions at which the analog and pulse modes will be used for subsequently collecting the spectral signal. The second analytical scan is then used for data collection; the system switches the detector back and forth rapidly between pulse and analog mode depending on the concentration of each analytical mass.

The main disadvantage of these two approaches is that two separate scans are required to measure high and low levels. With conventional nebulization, this isn’t such a major problem except that it can impact sample throughput. However, it does become a concern when it comes to working with transient peaks found in electrothermal vaporization, flow injection, or laser sampling ICP-MS. Because these transient peaks often last only a few seconds, all the available time must be spent measuring the masses of interest to get the best detection limits. When two scans have to be made, valuable time is
wasted, which is not contributing to quality of the analytical signal.

Using one scan with one detector. These limitations of using two scans led to the development of a third approach using a dual-stage discrete dynode detector (5). This technology uses measurement circuitry that allows both high and low concentrations to be determined in one scan. This is achieved by measuring the ion signal as an analog signal at the midpoint dynode. When more than a threshold number of ions are detected, the signal is processed through the analog circuitry. When fewer than the threshold number of ions are detected, the signal cascades through the rest of the dynodes and is measured as a pulse signal in the conventional way. This process, which is shown in Figure 3, is completely automatic and means that both the analog and the pulse signals are collected simultaneously in one scan (6).

The pulse-counting mode is typically linear from zero to about $10^6$ counts/s, while the analog circuitry is suitable from $10^4$ to $10^9$ counts/s. To normalize both ranges, a cross calibration is performed to cover concentration levels, which could generate a pulse and an analog signal. This is possible because the analog and pulse outputs can be defined in identical terms of incoming pulse counts per second, based on knowing the voltage at the first analog stage, the output current, and a conversion factor defined by the detection circuitry electronics. By performing a cross calibration across the mass range, a dual-mode detector of this type is capable of achieving approximately eight to nine orders of dynamic range in one simultaneous scan. Figure 4 shows the pulse-counting calibration curve (yellow) is linear up to $10^6$ cps, and the analog calibration curve (blue) is linear from $10^4$ to $10^9$ cps. Figure 5 shows that after cross calibration, the two curves are normalized, which means the detector is suitable for concentration levels between 0.1 ppt and 100 ppm — typically eight to nine orders of magnitude for most elements.

There are subtle variations of this type of detection system, but its major benefit is that it requires only one scan.

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Figure 4. The pulse-counting mode covers rates as high as $10^6$ counts/s, and the analog circuitry is suitable from $10^4$ to $10^9$ counts/s with a dual-mode discrete dynode detector.
to determine both high and low concentrations. Therefore, it not only offers the potential to improve sample throughput, it also means that the maximum data can be collected on a transient signal that only lasts a few seconds. This process will be described in greater detail in the next installment of this series, in which I will discuss different measurement protocols and peak integration routines.

References

Figure 5. Using cross calibration of the pulse and analog modes, quantitation from sub-part-per-trillion to high parts-per-million levels is possible.
A self-contained miniature x-ray tube system has been introduced by Amptek (Bedford, MA) for portable x-ray fluorescence (XRF) analysis. The LASER-X system houses the x-ray tube, power supply, and control electronics in a single, compact enclosure. Features include a grounded anode; variable current and voltage; a 35-kV, 100-μA power supply with a solid silver target; and an end window. The system is designed to replace radioisotopes in applications such as process control, OEM use, research, and teaching.

Bede (Englewood, CO) has just released the second version of its Instrument Control software, which offers an improved scripting engine, special applications screens, an improved scan set-up screen, and Windows 2000 compatibility. The company is also releasing new versions of its RADS and REFS software, which incorporate the company’s Mercury technology. Mercury uses genetic algorithms and provides an automatic parameter-optimization procedure for x-ray reflectivity and diffraction data. RADS 4.0 calculates high-resolution x-ray rocking curves for epitaxial crystal structures and substrates with Takagi-Taupin x-ray scattering equations of dynamical diffractions. REFS 4.0 employs the recursive formulation of dynamical theory for simulating grazing incidence x-ray reflectivity for both specular and diffuse and fluorescence curves.

The M4 Fluxer from Corporation Scientifique Claisse (Sainte-Foy, Quebec, Canada) is designed for preparing glass disks for XRF analysis. The system employs fusion to prepare oxides, sulfides, alloys, metal powders, and precious metals in the processing of cement, ores, slags, sediments, soils, rocks, ceramics, pigments, catalysts, ferroalloys, and other inorganic materials. Burners produce stable flames at a maximum temperature of 1630 °C. Gas settings of 30% and higher produce a linear increase in temperature, making the system easy to control. The fluxers are fused, homogenous, pure, and do not absorb moisture, according to the company.

DEL Electronics (Hicksville, NY) offers the XRD-3000 for x-ray diffraction (XRD) applications and the XRF-3000 for fluorescence. The 3-kW x-ray generators are compact and lightweight. They can be fully adjusted from the front panel or by remote control for beam voltage and emission current. The units contain an integrated filament supply and the control circuitry required for filamentary emission control. Users determine whether to use constant beam current or constant beam power modes. The company says it can tailor the systems to meet specific user requirements.

The Eagle III μ-Probe is the latest addition to the Eagle series of tabletop micro-XRF elemental analyzers from EDAX (Mahwah, NJ). The system uses capillary optics to concentrate the x-ray beam size down to a 100-μm diameter on the sample. Look-down, high-intensity x-ray optics, CCD video imaging cameras, and motorized xyz stage allow non-destructive, simultaneous Na–U analysis of solids, liquids, and powders. The analyzer offers an optic protection sensor and optional 30-mm² Si(Li) detector for spectral resolution of 80 mm². The Eagle III XPL μ-Probe equips the Eagle III with an x-ray polycapillary lens to generate an ultrahigh-intensity x-ray beam down to approximately a 40-μm diameter on the sample. It can be equipped with variable
spot size of 40 \( \mu m \) to 150 \( \mu m \) and automated primary filter control.

Three new products are available from distributor Handley Analytical Services (Houston, TX). UniQuant 5 is the latest version of Omega Data Systems’ software package for XRF spectrometers equipped with a goniometer. The software uses an extended form of the fundamental parameters method to overcome the problem of spectral line overlap. Graphic supported, weighted regression concentration is accompanied by an indication of a practical confidence interval for true quantitative analysis. Theoretical standard deviations are given based on counting errors and propagation of such errors due to line overlaps. Data collection is peak-based, so detection limits and accuracy for trace elements are comparable with those of conventional methods.

Handley also offers reengineered x-ray tubes made by Australian X-ray Tubes and XRF sample-preparation equipment from HD Elektronik und Elektrotechnik. Reengineered side-window tubes are available for a range of analyzers, including the Philips PW1400 series, Siemens SRS1 and SRS200, and Toshiba-compatible side-window tubes to fit Rigaku instruments. The tubes reportedly have several advantages over OEM tubes, such as improved vacuum and gettering and lower cost. They include a warranty comparable to that of new tubes.

The Vulcan2 and Vulcan4 automatic gas fusion machines are designed to provide highly flexible heating and cooling parameters, making them suitable for any mineral, ore, or ferroalloy sample preparation. The systems can reach temperatures as high as 1600 °C using standard propane. Two independently adjustable gas supplies for each burner give consistent and reproducible conditions of oxidation and fusion for each station.

Kratos Analytical (Chestnut Ridge, NY) has developed the XRF-1800 wavelength-dispersive sequential XRF spectrometer for qualitative and quantitative analysis. The instrument measures elements from Be to U in <3 min and performs local area analysis for wavelength-dispersive analysis. A high-sensitivity aperture and an accurate sample-positioning mechanism allow selected areas of the sample to be tested. The analysis area can be stepped down to 250 \( \mu m \), selected freely from within a 30-mm diameter area.

The company is also introducing the EDX-900 Benchtop EDXRF spectrometer, which uses a new thermoelectric cooling system to eliminate the need for liquid nitrogen. The instrument maintains the energy resolution of Si(Li) detectors, operates at \(-10 \) °C, and handles count rates as high as 10^6.

The new XRD-7000 x-ray diffractometer is designed to accommodate extra-large samples using a vertical 0–0 goniometer. The goniometer generates scan rates as high as 1000 °/min and provides angle reproducibility of 0.0002 °. The system supports analysis of samples in various states.

Materials Data, Inc. (MDI, Livermore, CA) is now shipping Jade 6.1, the latest version of its software for XRD powder pattern processing. The software’s new Xplorer feature finds and organizes all relevant XRD files from throughout an organization’s network. For XRD phase analysis, the software now includes a full physics phase-modeling option. The system supports Microsoft XP as well as previous Microsoft platforms.

Also new from MDI is Riqas 4, a stand-alone software tool for quantitative analysis using Rietveld methods that can be used to refine models against patterns to determine exact composition and atomic coordinates. FilmScan 3, new film acquisition software for film-based XRD analysis, is said to deliver the same level of automation to XRD films as electronic diffraction systems at a much lower price.
The new Bullet miniature x-ray tube from Moxtek (Orem, UT) is a compact x-ray source designed for low-power applications such as battery-operated, portable instruments. It features an integrated, high-voltage power supply that can provide 40 kV and 100 A of output with a maximum input power of 8 W. The design allows very close coupling of the source and sample, providing analytical results comparable to higher-powered x-ray tubes. The end-window version is available with a palladium or silver anode. Copper and tungsten anodes are available in a side-window configuration. The tube is available in 30- and 40-kV options.

Osmic (Auburn Hills, MI) has introduced the OV160Y boron analyzer, a multilayer system for the B–K radiation line. The system offers nearly double the intensity and peak-to-background ratios as the company’s previous Mo/B,C multilayer systems, it reports, and is approximately 20% improved over La/B,C multilayers.

Philips Analytical (Almelo, The Netherlands) has developed a new data platform for its X’Pert range of XRD software. Based on the new universal standard XML language, it offers users complete control over XRD measurement data. The new XRDML data platform stores ASCII-format XRD measurement data in XML-based files that contain all measurement data as well as information required to reproduce the data, including instrument type and settings, and it allows XRD system users to share measurements with others. The latest versions of X’Pert Data Collector, HighScore, and Epitaxy are available now; X’Pert Plus, Industry, and Stress will be released later this year.

MiniPal 2 is Philips Analytical’s newest benchtop EDXRF spectrometer. It performs nondestructive Na–U analysis in concentrations from 100% down to parts-per-million levels. The thermoelectrically cooled system analyzes liquids, powders, and surface coatings using an integrated deconvolution function that separates closely spaced peaks in the spectrum. A Microsoft Windows-based software can analyze a full range of elements without special accessories or modifications.

Pro-Trace is the latest addition to the company’s XRF SuperQ software for calculating net intensities in trace-element analysis down to sub-part-per-million levels. The system uses blank specimen and optional calibration standards with a calibrating power of more than 200 international standard reference materials. A Windows-based graphical user interface and available on-line help featuring worked examples simplify operation. The software is designed for use with the company’s MagiX, MagiX PRO, and MagiX FAST XRF systems.

Laser-X is a new industrial miniature x-ray source for XRF analysis from Photoelectron Corporation (Lexington, PA). The device is designed as an OEM replacement for the radioactive isotope sources used in hand-held XRF units and process-control monitors. According to the company, advantages of the new x-ray source over radioactive materials include the following:
• the radiation source can be turned on and off at will
• the intensity of the x-ray beam is consistently high, and
• the need for source replacement is eliminated.
Rigaku/MSC (The Woodlands, TX) is introducing the ZSX series of x-ray spectrometers designed for routine R&D. The ZSX101 is a full-size 4-kW production XRF spectrometer. The ZSX100s can be configured in a tube below or above, depending on the needs of the application. The ZSX mini is a benchtop WD-XRF system that operates at 110 V and does not require any cooling water for the tube or generator. It can be used for applications that don’t require a full-powered analyzer, or as a back-up for a larger WD-XRF unit. ZSX software incorporates the most advanced fundamental parameters software available, according to the company.

SPEX CertiPrep, Sample Preparation Division (Metuchen, NJ) introduces the 8000D and 8000M mixer/mills. Both are two-clamp laboratory mills featuring variable-range electronic timers, safety interlocks, and a wide choice of grinding and blending vials. The 8000D also offers forced-air cooling, has twice the capacity of its 8000 predecessor, and relies on two clamps that run in balance to provide smoother operation. Grinding/blending vials for both mills are available in hardened steel, stainless steel, tungsten carbide, agate, alumina ceramic, zirconia ceramic, acrylic, and polystyrene. The electronic timer range can be altered from 100 to 1000 min, making the mills suitable for lengthy operations such as mechanical alloying. The systems are designed for pulverizing rocks, cement, ceramics, and other materials in the 10-g range and for blending powders, paints, and emulsions in volumes as high as 60 mL or more. The high impact energy of the grinding balls has recently proved effective for mechanical alloying in the production of superconducting materials, the company reports.

Thermo NORAN, a Thermo Electron business (Middleton, WI), offers a complete new line of microbeam XRF metrology tools. MicronX systems feature collimated XRF tools that provide production-worthy film thickness and composition measurement of metal depositions for the microelectronics, telecommunications, data storage, and metal finishing industries. The systems measure the thickness and composition of as many as six layers of deposited metals simultaneously, from angstrom to micrometer thickness ranges. These systems can also determine bulk alloys for as many as 20 elements. The line includes several options, allowing systems to be optimized for specific applications. Features include mechanical or optical collimation, several x-ray detector options, and vacuum options. Using a common system platform and standardized subassemblies, each tool can be configured to deliver the best performance for the set of applications measured by the tool.

X-ray Instrumentation Associates (XIA, Newark, CA) introduces the /H9262 DXP, a credit card–sized, low-power, full-featured digital spectrometer for use in portable or embedded x-ray, gamma ray, and related applications. The system uses the company’s own gate array plus DSP technology to achieve impressive performance in a small size and at relatively low cost. Intended primarily for OEM and other large-volume, low-cost applications, the analyzer is supported by a suite of development tools including the /H9262 COM communication board and /H9262 MANAGER board setup and data collection software. The onboard DSP can support custom codes to carry out real-time spectral analysis and external equipment control functions. The system offers a choice of 4-, 8-, or 16-MSPS digitization rate, which sets basic power consumption (500, 630, or 750 mW) and maximum throughput (50, 100, or 200 kcps).

XIA is also introducing the Saturn, a completely digital x-ray spectrometer suitable for high-rate and high-resolution applications. The newest member of the DXP line, the Saturn is intended for industrial and laboratory
Modern ICP-MS must be very flexible to meet such diverse application needs and keep up with the increasing demands of its users. Nowhere is this more important than in the area of peak integration and measurement protocol. The way the analytical signal is managed in ICP-MS directly impacts its multielement capability, detection limits, dynamic range, and sample throughput—the four major strengths that attracted the trace element community to the technique almost 20 years ago. To understand signal management and its implications on data quality in greater detail, this installment of this series will discuss how measurement protocol is optimized based on the application’s analytical requirements. I will discuss its impact on both continuous signals generated by traditional nebulization devices and transient signals produced by alternative sample introduction techniques such as flow injection and laser ablation.

### Measurement Variables

Many variables affect the quality of the analytical signal in ICP-MS. The analytical requirements of the application will often dictate this factor, but instrumental detection and measurement parameters can have a significant impact on the quality of data in ICP-MS. Some of the variables that can affect the quality of your data, particularly when carrying out multielement analysis, include:

- whether the signal is continuous or transient
- the temporal length of the sampling event
- the volume of sample available
- the number of samples being analyzed
- the number of replicates per sample
- the number of elements being determined

Before discussing these factors in greater detail, and how they affect data quality, it is important to remember how a scanning device such as a quadrupole mass analyzer works. Although we will focus on quadrupole technology, the fundamental principles of measurement protocol will be very similar for all types of mass spectrometers that use a scanning approach for multielement peak quantitation.

### Measurement Protocol

Figure 1 shows the principles of scanning with a quadrupole mass analyzer. 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 will pass through the spaces between the rods and be ejected from the quadrupole. This scanning process is then repeated for another analyte at a completely different mass-to-charge ratio.
Tutorial

The process for detecting one particular mass in a multielement run is represented in Figure 2, which shows a $^{63}\text{Cu}$ 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 $^{63}\text{Cu}$ — 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 $^{63}\text{Cu}$. 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.

The principles of multielement peak acquisition are shown in Figure 3. In this example (showing two masses), signal pulses are continually collected as the quadrupole is swept across the mass spectrum (in this case three times). After a given number sweeps, the total number of signal pulses in each channel are counted.

When it comes to quantifying an isotopic signal in ICP-MS, there are basically two approaches to consider (2). One is the multichannel ramp scanning approach, which uses a continuous smooth ramp of 1 to $n$ channels (where $n$ is typically 20) per mass across the peak profile. This approach is shown in Figure 4.

The peak-hopping approach is where the quadrupole power supply is driven to a discrete position on the peak (normally the peak point) and allowed to settle; a measurement is then taken for a fixed amount of time. This approach is represented in Figure 5.

The multipoint scanning approach is best for accumulating spectral and peak shape information when doing mass scans. It is normally used for doing mass calibration and resolution checks, and as a classical qualitative method development tool to find out what elements are present in the sample, as well as to assess their spectral implications on the masses of interest. Full peak profiling is not normally used for doing rapid quantitative analysis because valuable analytical time is wasted taking data on the wings and valleys of the peak, where the signal-to-noise ratio is poorest.

When the best possible detection limits are required, the peak-hopping approach is best. It is important to understand that, to get the full benefit of peak hopping, the best detection limits are achieved when single-point peak hopping at the peak maximum is chosen. However, to carry out single-point peak hopping, it is essential that the mass stability is good enough to reproducibly go to the same mass point every time. If good mass stability can be guaranteed (usually by thermostating the quadrupole power supply), measuring the signal at the peak maximum will always give the best detection limits for a given integration time. It is well documented that there is no benefit to spreading the chosen integration time over more than one measurement point per mass. If time is a major consideration in the analysis, then using multiple points is wasting valuable time on the wings and valleys of the peak, which contribute less to the analytical signal.
Figure 3 (above left). A profile of the peak is built up by continually sweeping the quadrupole across the mass spectrum.

Figure 4 (above right). Multichannel ramp scanning approach using 20 channels per amu.

Figure 5 (below right). Peak-hopping approach.

and more to the background noise. Figure 6 shows the degradation in signal-to-background noise ratio of 10 ppb Rh with an increase in the number of points per peak, spread over the same total integration time. Detection limit improvement for a selected group of elements using 1 point/peak, rather than 20 points/peak, is shown in Figure 7.

**Optimization of Measurement Protocol**

Now that the fundamentals of the quadrupole measuring electronics have been described, let us now go into more detail on the impact of optimizing the measurement protocol based on the requirement of the application. When multielement analysis is being carried out by ICP-MS, a number of decisions need to be made. First, we need to know if we are dealing with a continuous signal from a nebulizer or a transient signal from an alternative sampling accessory. If it is a transient event, how long will the signal last? Another question that needs to be addressed is, how many elements are going to be determined? With a continuous signal, this isn’t such a major problem, but it could be an issue if we are dealing with a transient signal that lasts a few seconds. We also need to be aware of the level of detection capability required. This is a major consideration with a single-shot laser pulse that lasts 5–10 s. Also with a continuous signal produced by a concentric nebulizer, we might have to accept a compromise of detection limit based on the speed of analysis requirements or amount of sample available. What analytical precision is expected? If it’s isotope ratio/dilution work, how many ions do we have to count to guarantee good precision? Does increasing the integration time of the measurement help the precision? Finally, is there a time constraint on the analysis? A high-throughput laboratory might not be able to afford to use the optimum sampling time to get the ultimate in detection limit. In other words, what compromises need to be made between detection limit, precision, and sample throughput? Clearly, before the measurement protocol can be optimized, the major analytical requirements of the application need to be defined. Let’s take a look at this process in greater detail.

**Multielement Data Quality Objectives**

Because multielement detection capability is probably the major reason why

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<th>Dwell time (ms)</th>
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<tr>
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<td>0.24</td>
<td>0.25</td>
</tr>
<tr>
<td>50</td>
<td>0.38</td>
<td>0.33</td>
</tr>
<tr>
<td>100</td>
<td>0.41</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Signal-to-background noise ratio degrades when more than one point, spread over the same integration time, is used for peak quantitation.

Detection limit improvement using 1 point/peak rather than 20 points/peak over the mass range.

Figure 6. Signal-to-background noise ratio degrades when more than one point, spread over the same integration time, is used for peak quantitation.

Figure 7. Detection limit improvement using 1 point/peak rather than 20 points/peak over the mass range.

and then dwell on the peak, or sit, and take measurements for a fixed period of time. This step is usually performed a number of times until the total integration time is fulfilled. For example, if a dwell time of 50 ms is selected for all masses and the total integration time is 1 s, then the quadrupole will carry out 20 complete sweeps per mass, per replicate. It will then repeat the same routine for as many replicates that have been built into the method. This process is illustrated very simplistically in Figure 8, which shows the scanning protocol of a multielement scan of three different masses.

In this example, the quadrupole is scanned to mass A. The electronics are allowed to settle (settling time) and left to dwell for a fixed period of time at one or multiple points on the peak (dwell time); intensity measurements are then taken (based on the dwell time). The quadrupole is then scanned to masses B and C and the measurement protocol repeated. The complete multielement measurement cycle (sweep) is repeated as many times as needed to make up the total integration per peak. It should be emphasized that this example is a generalization of the measurement routine — management of peak integration by the software will vary slightly, based on different instrumentation.

It is clear from this information that, during a multielement analysis, a significant amount of time is spent scanning and settling the quadrupole, which doesn’t contribute to the quality of the analytical signal. Therefore, if the measurement routine is not optimized carefully, it can have a negative impact on data quality. The dwell time can usually be selected on an individual mass basis, but the scanning and settling times are normally fixed because they are a function of the quadrupole and detector electronics. For this reason, it is essential that the dwell time — which ultimately affects detection limit and precision — must dominate the total measurement time, compared with the scanning and settling times. It follows, therefore, that the measurement duty cycle (percentage of actual measuring time compared with total integration time) is maximized when the quadrupole and detector electronics settling times are kept to an absolute minimum.

Figure 9 shows a plot of percentage of measurement efficiency against dwell time per mass. Although 1 s is long enough to achieve reasonably good detection limits, longer integration times generally have to be used to reach the

<table>
<thead>
<tr>
<th>Element</th>
<th>#Elements</th>
<th>#Replicates</th>
<th>#Sweeps</th>
<th>Scanning / Settling Time</th>
<th>Dwell Time</th>
<th>Measurement Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be-9</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>0.2, 1.0, 3.0, 5.0 ms</td>
<td>1 s</td>
<td>0.95</td>
</tr>
<tr>
<td>Co-59</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>0.2, 1.0, 3.0, 5.0 ms</td>
<td>1 s</td>
<td>0.95</td>
</tr>
<tr>
<td>In-115</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>0.2, 1.0, 3.0, 5.0 ms</td>
<td>1 s</td>
<td>0.95</td>
</tr>
<tr>
<td>Tl-205</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>0.2, 1.0, 3.0, 5.0 ms</td>
<td>1 s</td>
<td>0.95</td>
</tr>
<tr>
<td>U-238</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>0.2, 1.0, 3.0, 5.0 ms</td>
<td>1 s</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Dwell Time × #Sweeps × #Elements × #Replicates × 100

= Measurement Efficiency

Scanning / Settling Time × #Sweeps × #Elements × #Replicates

So to achieve the highest measurement efficiency, the nonanalytical time must be kept to an absolute minimum. This leads to more time being spent counting ions and less time scanning and settling, which does not contribute to the quality of the analytical signal. This factor becomes critically important when a rapid transient peak is being quantified, because the available measuring time is that much shorter (3). Generally speaking, peak quantitation using multiple points per peak and long settling times should be avoided in ICP-MS because it ultimately degrades the quality of the data for a given integration time.

Figure 9 also shows that shorter dwell times translate into a lower measurement efficiency. For this reason, it is probably desirable, for normal quantitative analysis work, to carry out multiple sweeps with longer dwell times (typically 50 ms) to get the best detection limits. So if an integration time of 1 s is used for each element, this would translate into 20 sweeps of 50 ms dwell time per mass. Although 1 s is long enough to achieve reasonably good detection limits, longer integration times generally have to be used to reach the
lowest possible detection limits. Figure 10 shows detection limit improvement as a function of integration time for $^{238}$U. As would be expected, there is a fairly predictable improvement in the detection limit as the integration time is increased because more ions are being counted without an increase in the background noise. However, this only holds true up to the point where the pulse-counting detection system becomes saturated and no more ions can be counted. In the case of $^{238}$U, this occurs around 25 s, because there is no obvious improvement in detection limit at a higher integration time. So from these data, we can say that there appears to be no real benefit in using an integration time longer than 7 s. When deciding the length of the integration time in ICP-MS, you have to weigh the detection limit improvement against the time taken to achieve that improvement. Is it worth spending 25 s measuring each mass to get a 0.02 ppt detection limit if 0.03 ppt can be achieved using a 7-s integration time? Alternatively, is it worth measuring for 7 s when 1 s will only degrade the performance by a factor of 3? It really depends on your data quality objectives.

For applications such as isotope dilution/ratio studies, high precision is also a very important data quality objective (4). However, to understand what is realistically achievable, we must be aware of the practical limitations of measuring a signal and counting ions in ICP-MS. Counting statistics tells us that the standard deviation of the ion signal is proportional to the square root of the signal. It follows, therefore, that the relative standard deviation (RSD), or precision, should improve with an increase in the number (N) of ions counted as shown by the following equation:

$$\%\text{RSD} = \frac{\sqrt{N}}{N} = 100$$

In practice this holds up very well, as shown in Figure 11. In this plot of standard deviation as a function of signal intensity for $^{208}$Pb, the dots represent the theoretical relationship as predicted by counting statistics. It can be seen that the measured standard deviation (bars) follows theory very well up to about 100,000 cps. At that point, additional sources of noise (for example, sample introduction pulsations or plasma fluctuations) dominate the signal, which leads to poorer standard deviation values.

So based on counting statistics, it is logical to assume that the more ions that are counted, the better the precision will be. To put this in perspective, it means that at least 1 million ions need to be counted to achieve an RSD of 0.1%. In practice, of course, these kinds of precision values are very difficult to achieve with a scanning quadru-

### Table II. Impact of integration time on the overall analysis time for Pb isotope ratios.

<table>
<thead>
<tr>
<th>Dwell time (ms)</th>
<th>Number of sweeps</th>
<th>Integration time (s)/mass</th>
<th>$%\text{RSD, } ^{207}\text{Pb}/^{206}\text{Pb}$ for 9 reps</th>
<th>Analysis time</th>
<th>$%\text{RSD, } ^{208}\text{Pb}/^{206}\text{Pb}$</th>
<th>$%\text{RSD, } ^{207}\text{Pb}/^{206}\text{Pb}$ for 9 reps</th>
<th>Analysis time</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>220</td>
<td>5.5</td>
<td>0.24</td>
<td>2 min 29 s</td>
<td>0.25</td>
<td>0.17</td>
<td>8 min 29 s</td>
</tr>
<tr>
<td>25</td>
<td>500</td>
<td>12.5</td>
<td>0.21</td>
<td>6 min 12 s</td>
<td>0.19</td>
<td>0.17</td>
<td>8 min 29 s</td>
</tr>
<tr>
<td>25</td>
<td>700</td>
<td>17.5</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
pole system because of the additional sources of noise. If this information is combined with our knowledge of how the quadrupole is scanned, we begin to understand what is required to get the best precision. This is confirmed by the spectral scan in Figure 12, which shows the predicted precision at all 20 channels of a 5 ppb 208Pb peak (2).

Therefore, the best precision is obtained at the channels where the signal is highest, which as we can see are the ones at or near the center of the peak. For this reason, if good precision is a fundamental requirement of your data quality objectives, it is best to use single-point peak hopping with integration times in the order of 5–10 s. On the other hand, if high-precision isotope ratio or isotope dilution work is being done — in which analysts would like to achieve precision values approaching counting statistics — then much longer measuring times are required. That is why integration times of 5–10 min are commonly used for determining isotope ratios with a quadrupole ICP-MS system (5, 6). For this type of analysis, when two or more isotopes are being measured and ratioed to each other, it follows that the more simultaneous the measurement, the better the precision becomes. Therefore, the ability to make the measurement as simultaneous as possible is considered more desirable than any other aspect of the measurement. This is supported by the fact that the best isotope ratio precision data are obtained with time-of-flight or multicollector, magnetic sector ICP-MS systems, which are both considered simultaneous in nature. So the best way to approximate simultaneous measurement with a rapid scanning device, such as a quadrupole, is to use shorter dwell and scanning/settling times, resulting in more sweeps for a given integration time. Table I shows precision of Pb isotope ratios at different dwell times carried out by researchers at the Geological Survey of Israel (7). The data are based on nine replicates of a NIST SRM-981 (75 ppb Pb) solution, using 5.5 s of integration time per isotope. From these data, the researchers concluded that a dwell time of 10 or 25 ms offered the best isotope ratio precision measurement (quadrupole settling time was fixed at 0.2 ms). They also found that they could achieve slightly better precision by using a 17.5-s integration time (700 sweeps at a 25-ms dwell time), but felt the marginal improvement in precision for nine replicates was not worth spending the approximately 3.5-times-longer analysis time, as shown in Table II.

This work shows the benefit of optimizing the dwell time, settling time, and the number of sweeps to get the best isotope ratio precision data. The researchers were also very fortunate to be dealing with relatively healthy signals for the three Pb isotopes, 206Pb, 207Pb, and 208Pb (24.1%, 22.1%, and 52.4% abundance, respectively). If the isotopic signals were dramatically different like in 235U to 238U (0.72 % and 99.2745% abundance, respectively), then the ability to optimize the measurement proto-
col for individual isotopes becomes of even greater importance to guarantee precise data.

It is clear that the analytical demands put on ICP-MS are probably higher than any other trace element technique because it is continually being asked to solve a wide variety of application problems. However, by optimizing the measurement protocol to fit the analytical requirement, ICP-MS has shown that it has the capability to carry out rapid trace element analysis, with superb detection limits and good precision on both continuous and transient signals, and still meet the most stringent data quality objectives.

References