Beginner's Guide to ICP-MS

Part VI — The Mass Analyzer

ROBERT THOMAS

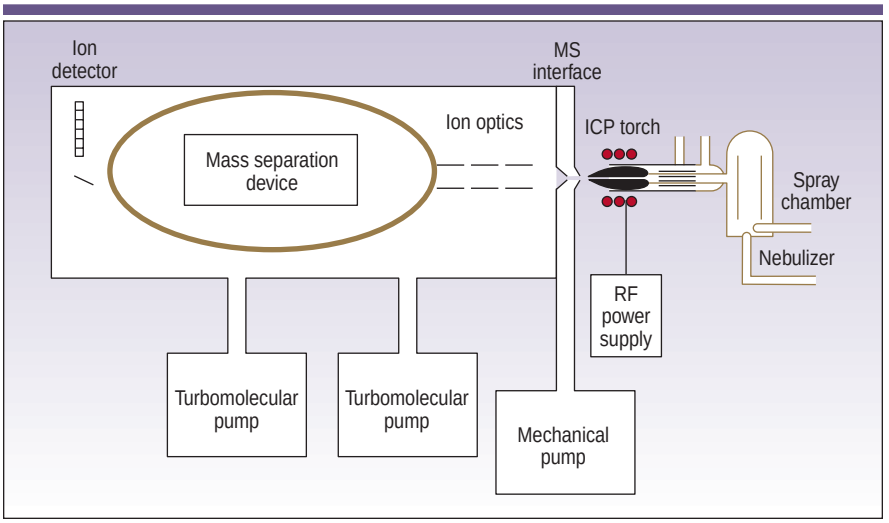

Figure 1. Schematic of an ICP-MS system showing the location of the mass separation device.

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

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

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

QUADRUPOLE MASS FILTER TECHNOLOGY

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

BASIC PRINCIPLES OF OPERATION

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

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

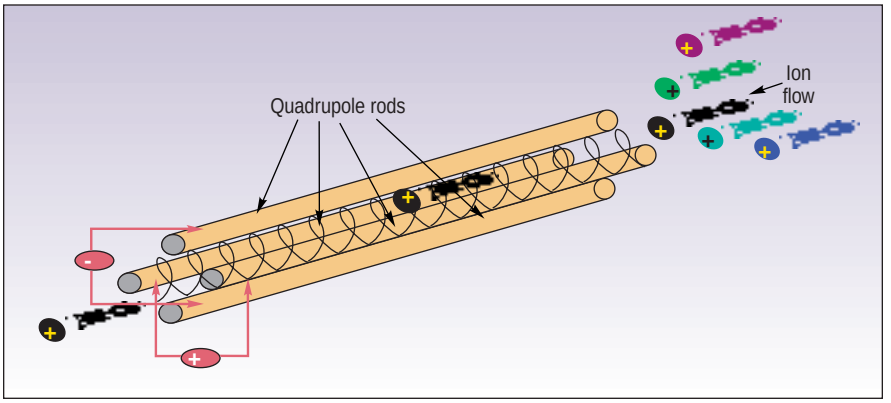

Figure 2. Schematic showing principles of a quadrupole mass filter.

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

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

QUADRUPOLE PERFORMANCE CRITERIA

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

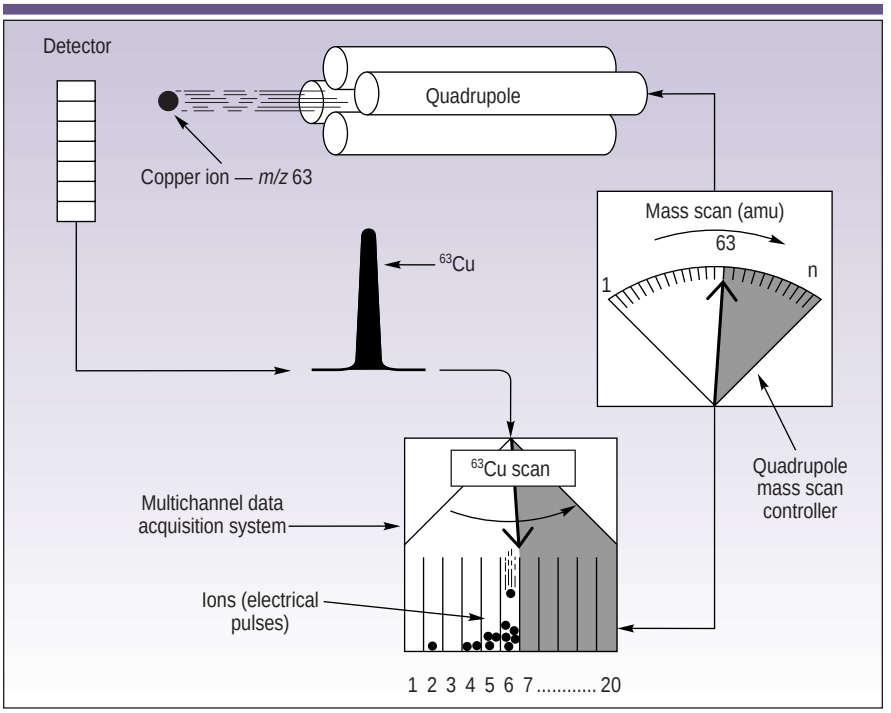

Figure 3. Profiles of different masses are built up using a multichannel data acquisition system.

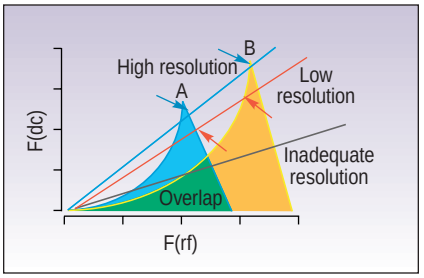

Figure 4. Simplified Mathieu stability diagram of a quadrupole mass filter, showing separation of two different masses, *A* (light blue plot) and *B* (yellow plot).

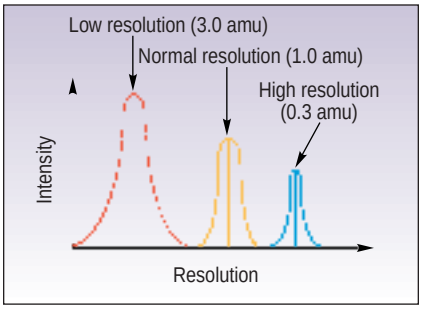

Figure 5. Sensitivity comparison of a quadrupole operated at 3.0, 1.0, and 0.3 amu resolution (measured at 10% of its peak height).

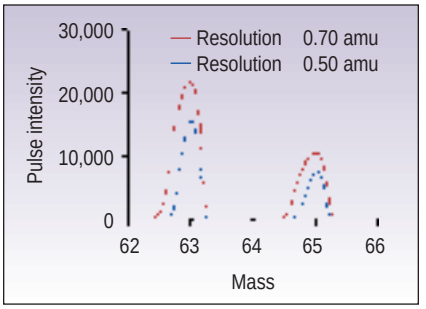

Figure 6. Sensitivity comparison of two copper isotopes, ^{63}Cu and ^{65}Cu, at resolution settings of 0.70 and 0.50 amu.

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

RESOLUTION

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

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

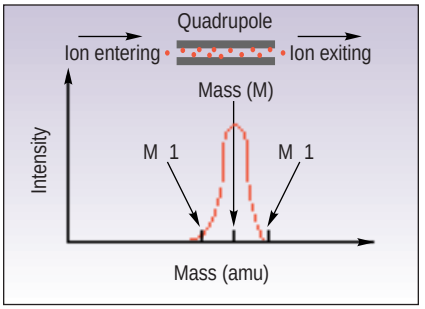

Figure 7. Ions entering the quadrupole are slowed down by the filtering process and produce peaks with a pronounced tail or shoulder at the low-mass end.

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

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

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

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

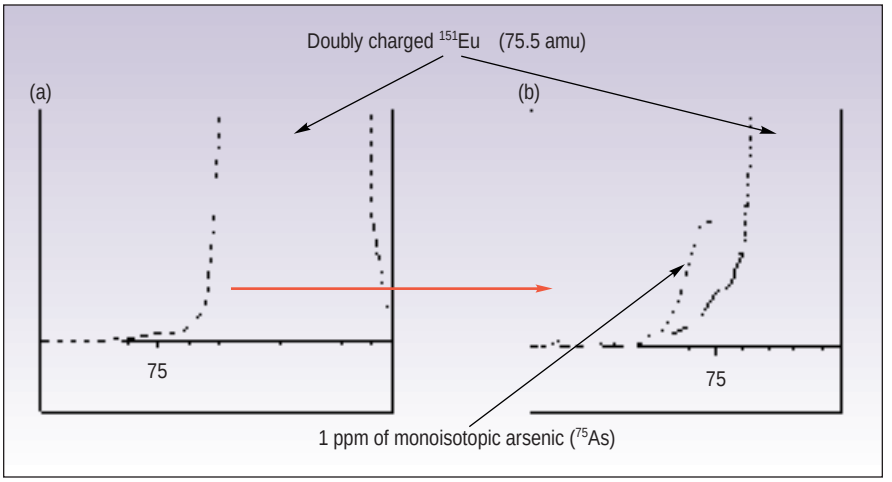

Figure 8. A low abundance sensitivity specification is critical to minimize spectral interferences, as shown by (a) a spectral scan of 50 ppm of $^{151}Eu^{++}$ at 75.5 amu and (b) an expanded view, which shows how the tail of the $^{151}Eu^{++}$ elevates the spectral background of 1 ppb of As at mass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

ABUNDANCE SENSITIVITY

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

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

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

BENEFITS OF GOOD ABUNDANCE SENSITIVITY

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

DIFFERENT QUARDUPOLE DESIGNS

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

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

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