

# A Beginner's Guide to ICP-MS

## Part VII: Mass Separation Devices — Double-Focusing Magnetic-Sector Technology

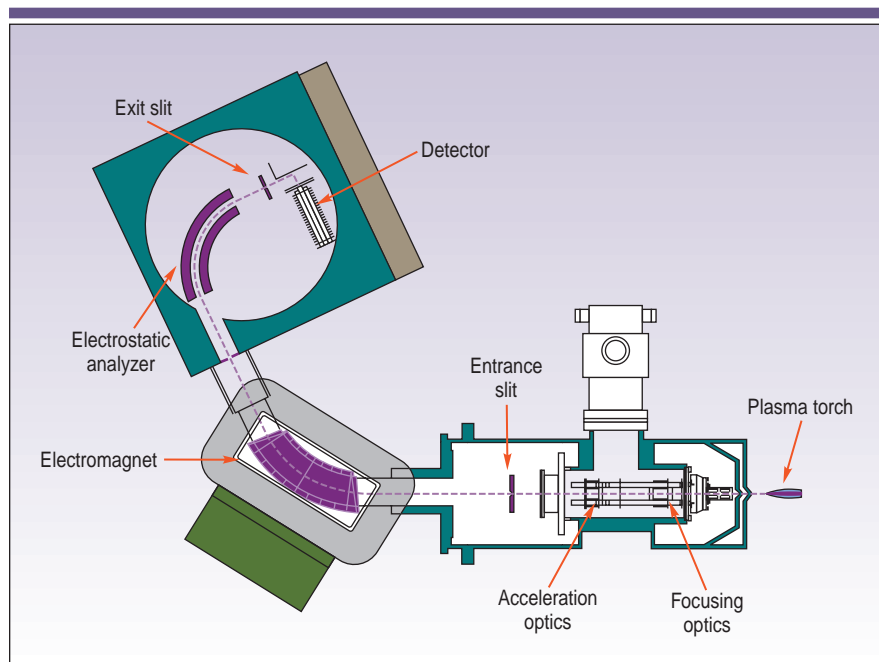
ROBERT THOMAS

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



**Figure 1.** Schematic of a reverse Nier-Johnson double-focusing magnetic-sector mass spectrometer (Courtesy of Thermo Finnigan [San Jose, CA]).

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 ana-

lyzers — 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 with diverging angles of motion from the entrance slit. The ESA, which is only dispersive with respect to ion energy, then fo-

causes the ions onto the exit slit, where the detector is positioned. If the energy dispersion of the magnet and ESA are equal in magnitude but opposite in direction, they will focus both ion angles (first focusing) and ion energies (second or double focusing), when combined together. Changing the electrical field in the opposite direction during the cycle time of the magnet (in terms of the mass passing the exit slit) has the effect of freezing the mass for detection. Then as soon as a certain magnetic field strength

**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.**

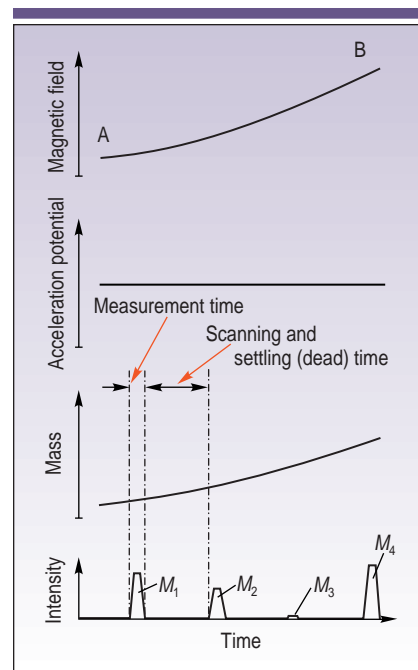
is passed, the electric field is set to its original value and the next mass is frozen. The voltage is varied on a per-mass basis, allowing the operator to scan only the mass peaks of interest rather than the full mass range (3, 4).

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

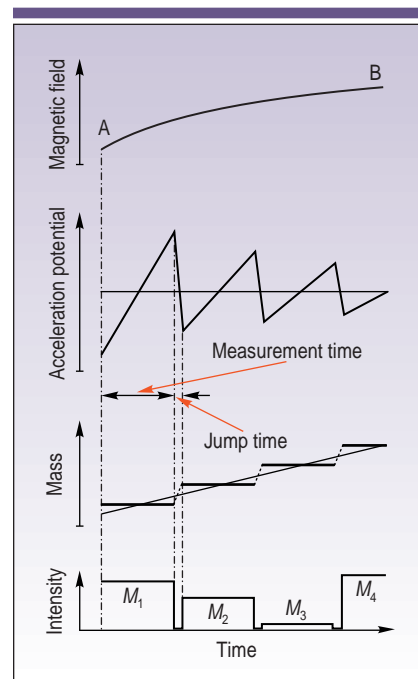
magnet. This was not such a major problem for qualitative analysis, but proved to be impractical for routine trace element analysis. This concept is shown in greater detail in Figure 2, which is a plot of four parameters — magnetic field strength, accelerating voltage, mass, and signal intensity — against 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. Then, as soon as the magnetic field strength is passed, the electrical field is set to its original value and the next mass “stopped” in the same manner. The accelerating voltage, as well as its rate of change, has to be varied depending on the mass, but the benefit of this method is that only the mass peaks of interest are registered. This process is seen in Figure 3, which shows the same four masses scanned. The only difference this time is that as well as scanning the magnet from point A to point B, the accelerating voltage is also changed, resulting in a step-wise jump from one mass to the next. This means that the full mass range is covered much faster than just by scanning the magnet alone (because of the increased speed involved in electrically jumping from one mass to another) (5). Once the magnet has been scanned to a particular point, an electric scan is used to cover an area of  $\pm 10$ – $30\%$  of the mass, either to measure the analyte peak or monitor other masses of interest. Peak quantitation is typically performed by taking multiple data points over a preset mass window and integrating over a fixed period of time.

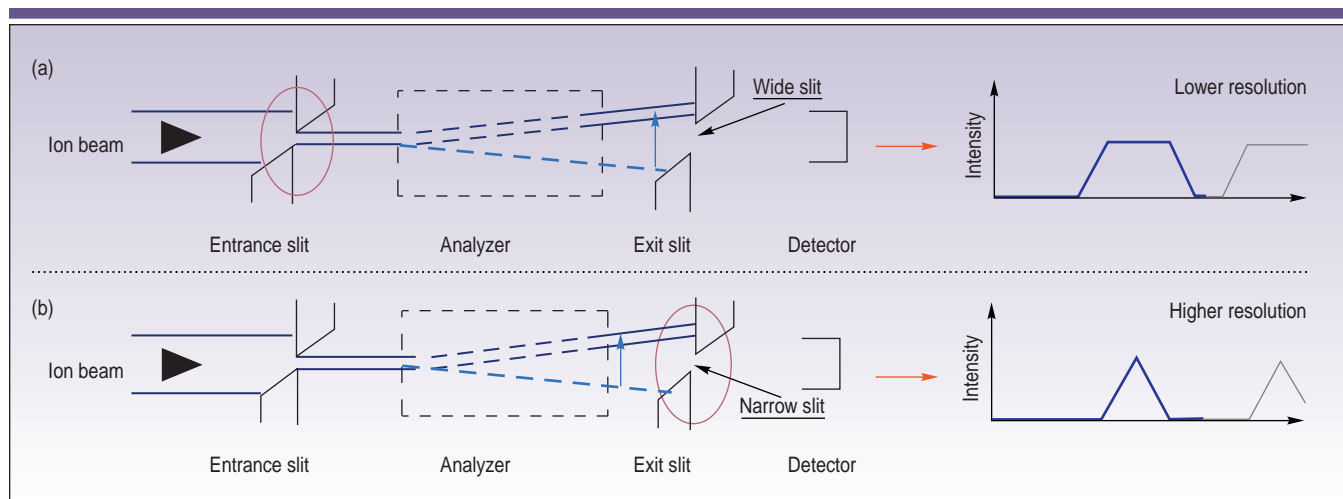
It should be pointed out that although this approach represents enormous time savings over older, single-focusing magnetic-sector technology, it is still significantly slower than quadrupole-based instruments. The inherent problem lies in the fact that a quadrupole can be electrically scanned much faster than a



**Figure 2.** A plot of magnetic field strength, accelerating voltage (fixed), mass, and signal intensity over time for four separate masses ( $M_1$ – $M_4$ ). Note that only the magnet is scanned, while the accelerating voltage is fixed — resulting in long scan times between the masses.



**Figure 3.** A plot of magnetic field strength, accelerating voltage (changed), mass, and signal intensity over time for the same four masses ( $M_1$ – $M_4$ ). This time, in addition to the magnet being scanned, the accelerating voltage is also changed, resulting in rapid electric jumps between the masses.



**Figure 4.** Resolution obtained using (a) wide and (b) narrow exit slit widths as the magnetic field is scanned. The entrance slit widths are the same in (a) and (b).

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 commer-

cial 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:  $R = m/\Delta m$ , 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

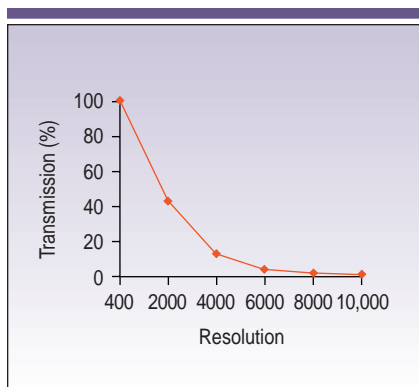
field under different entrance- and exit-slit width conditions. Similar to optical systems, low resolution is achieved by using wide slits, whereas high resolution is achieved with narrow slits. Varying the width of both the entrance and exit slits effectively changes the operating resolution. This can 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.

Isotope	Matrix	Interference	Resolution	Transmission
<sup>39</sup> K	H <sub>2</sub> O	<sup>38</sup> ArH	5570	6%
<sup>40</sup> Ca	H <sub>2</sub> O	<sup>40</sup> Ar	199,800	0%
<sup>44</sup> Ca	HNO <sub>3</sub>	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	970	80%
<sup>56</sup> Fe	H <sub>2</sub> O	<sup>40</sup> Ar <sup>16</sup> O	2504	18%
<sup>31</sup> P	H <sub>2</sub> O	<sup>15</sup> N <sup>16</sup> O	1460	53%
<sup>34</sup> S	H <sub>2</sub> O	<sup>16</sup> O <sup>18</sup> O	1300	65%
<sup>75</sup> As	HCl	<sup>40</sup> Ar <sup>35</sup> Cl	7725	2%
<sup>51</sup> V	HCl	<sup>35</sup> Cl <sup>16</sup> O	2572	18%
<sup>64</sup> Zn	H <sub>2</sub> SO <sub>4</sub>	<sup>32</sup> S <sup>16</sup> O <sup>16</sup> O	1950	42%
<sup>24</sup> Mg	Organics	<sup>12</sup> C <sup>12</sup> C	1600	50%
<sup>52</sup> Cr	Organics	<sup>40</sup> Ar <sup>12</sup> C	2370	20%
<sup>55</sup> Mn	HNO <sub>3</sub>	<sup>40</sup> Ar <sup>15</sup> N	2300	20%





**Figure 5.** Ion transmission with a magnetic-sector instrument decreases as the resolution increases.

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 —  $^{40}\text{Ar}^{16}\text{O}$  on  $^{56}\text{Fe}$ , which requires a resolution of 2504 to separate the peaks. Figure 6a shows a spectral scan of  $^{56}\text{Fe}$  using a quadrupole instrument. What it doesn't show is the massive polyatomic interference  $^{40}\text{Ar}^{16}\text{O}$  (produced by oxygen ions from the water combining with argon ions from the plasma) completely overlapping the  $^{56}\text{Fe}$ . 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

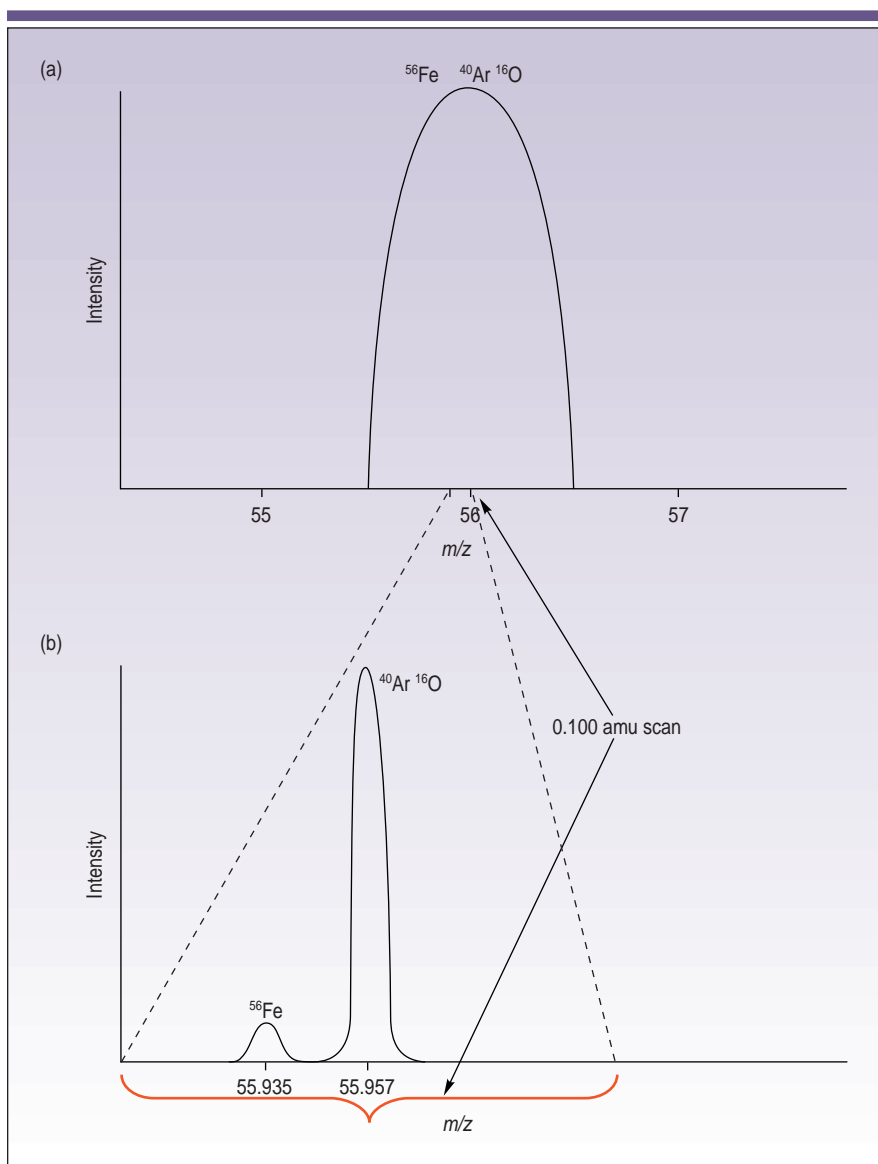
Besides high resolving power, another attractive feature of magnetic-sector instruments is their very high sensitivity combined with extremely low background levels. High ion transmission in low-resolution mode translates into sensitivity specifications of typically 100–200 million counts per second (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  $\sim 10$  cps for a quadrupole instrument. For this reason detection limits, es-

pecially 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,



**Figure 6.** Comparison of resolution between (a) a quadrupole and (b) a magnetic-sector instrument for the polyatomic interference of  $^{40}\text{Ar}^{16}\text{O}$  on  $^{56}\text{Fe}$ .

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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).

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**Robert Thomas** has more than 30 years of 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](mailto:thomasrj@bellatlantic.net) or via his web site at [www.scientificsolutions1.com](http://www.scientificsolutions1.com). ♦

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