A Beginner's Guide to ICP-MS

Part VIII — Mass Analyzers: Time-of-Flight Technology

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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

$$E_k = \tfrac{1}{2}mv^2 \qquad [1]$$

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

$$m/z = 2Ut^2/D^2 \qquad [2]$$

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
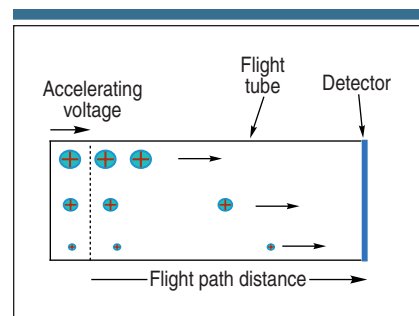

Figure 1. Principles of ion detection using TOF technology, showing separation of three masses in the time domain.

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-

ent masses are then resolved in the time domain in a similar manner to the orthogonal design. The layout of an on-axis TOF system is shown schematically in Figure 3.

Figures 2 and 3 represent a rather simplistic 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 components 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 interface. These packets of ions are then directed toward a deflection–steering plate where pulsed voltages steer the ions (or throw out unwanted species) in the direction of a reflectron. The packets of ions are then deflected back 180°, where they are detected by a channel electron multiplier or discrete dynode detector. The reflectron is a type of ion mirror and functions as an energy compensation device, so that different ions of the same mass arrive 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 intent of this tutorial to make any personal judgement about the benefits or disadvantages 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 greatest energy dispersion is along the axis of the flight tube. In addition, when ions are extracted orthogonally, the energy dispersion can produce angular divergence of the ion beam resulting in poor transmission efficiency. However, the sensitivity of either TOF design is still generally
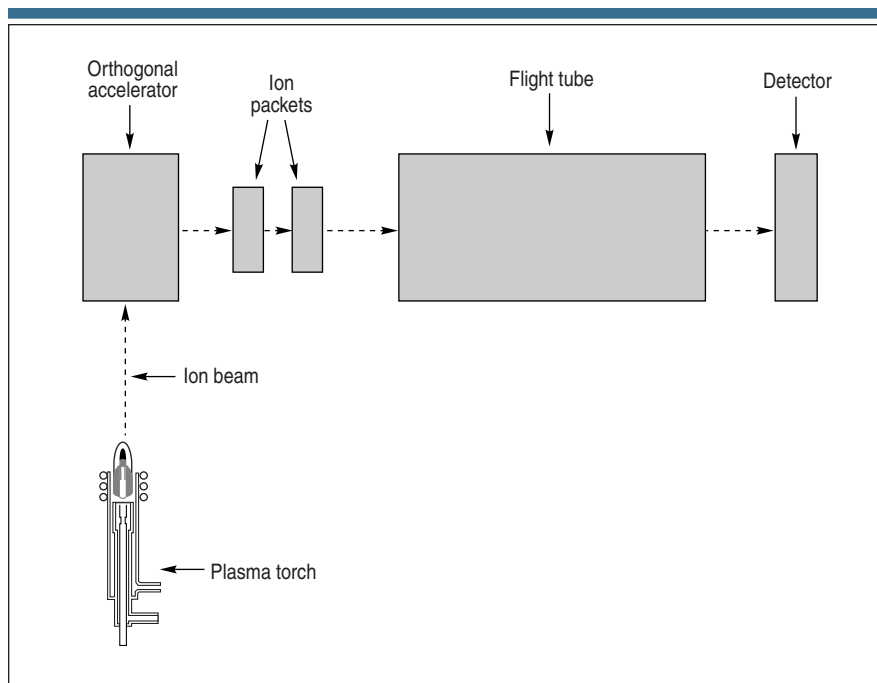

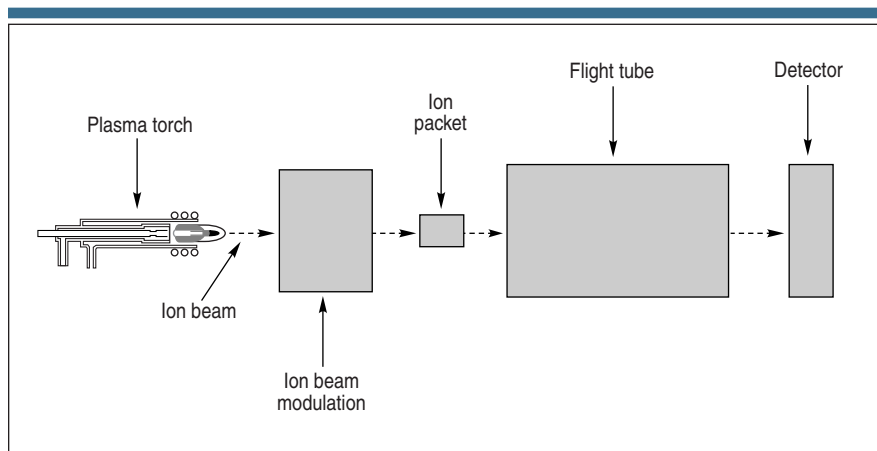**Figure 2.** Schematic of an orthogonal acceleration TOF analyzer.

Figure 3. Schematic of an on-axis acceleration TOF analyzer.

lower than the latest commercial quadrupole instruments.

Background levels. The on-axis design tends to generate higher background levels because neutral species and photons stand a greater chance of reaching the detector. This results in background levels 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 commercial 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 emphasized that even though the ions are sampled at the same time, detection is not simultaneous 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.
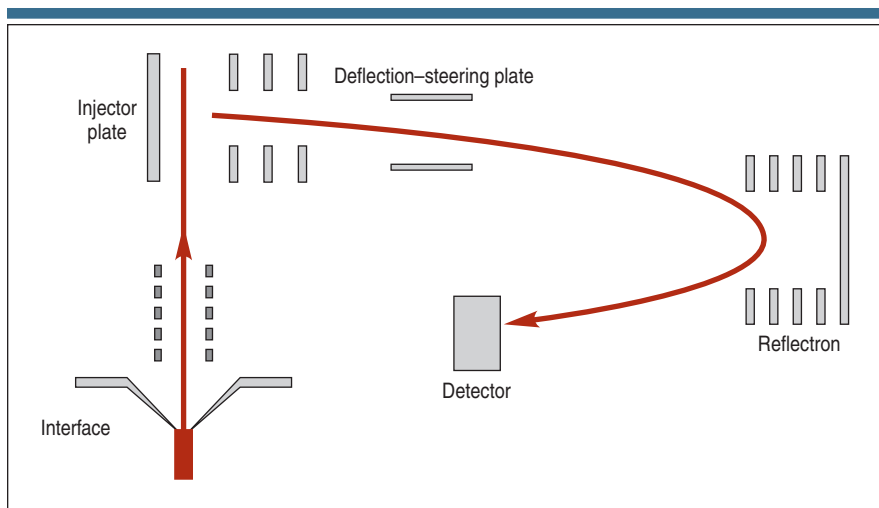
Figure 4. A more detailed view of a typical orthogonal TOF analyzer, showing some of the ion steering components.
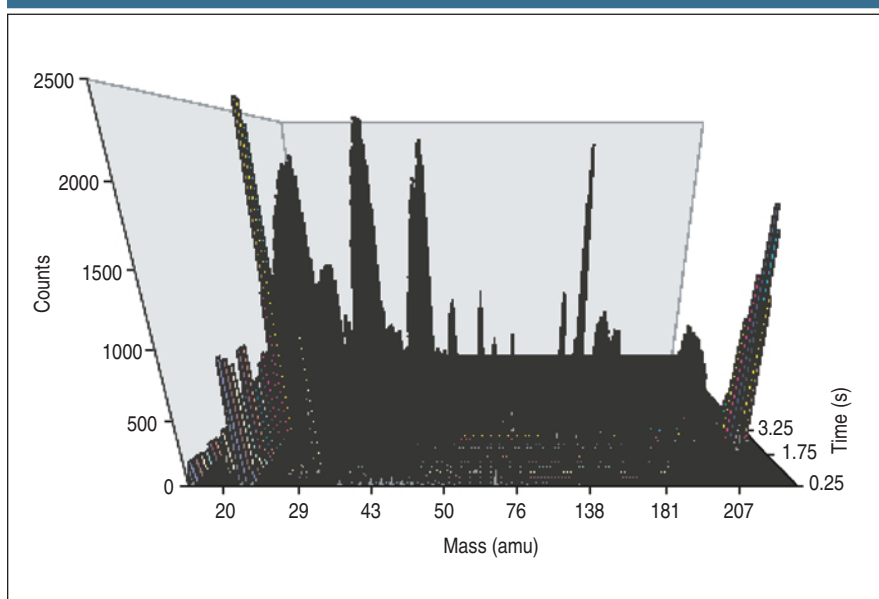

Figure 5. A full mass scan of a transient signal generated by 10 μL of a 5-ppb multielement solution using an electrothermal vaporization sampling accessory coupled to a TOF ICP-MS system (courtesy of GBC Scientific Equipment [Arlington Heights, IL]).

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 res-

olution. 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

Correction

In reference to Part VII of my tutorial series, "A Beginner's Guide to ICP-MS," which was published in the November 2001 issue of *Spectroscopy*, I would like to make a number of corrections. Even though the intent of the article was to give a general overview of double-focusing magnetic-sector mass analyzers for beginners, Thermo Finnigan contacted *Spectroscopy* to inform the editors and me that the column contained errors, and that it did not reflect the current performance of their instrument, the ELEMENT2. For that reason, I wish to make the following amendments to the article.

• My statement that double-focusing magnetic sector ICP-MS instruments are significantly slower than quadrupole technology does not hold true today. Recent improvements in the scan rate of the ELEMENT2 translates into speeds approaching that of quadrupole-based instruments.

• My statement that typical scan speeds for a full mass scan were 400–500 ms is reflective of older magnetic sector technology. This is not representative of the ELEMENT2, which has a scan speed in the order of 150–200 ms.

• My statement that typical sensitivity was in the order of 100–200 million cps/ppm is not reflective of the ELEMENT2, which has a specification for 115In of 1 billion cps/ppm.

• My conclusion should therefore be modified to say that if transient peak analysis is a requirement, modern double-focusing magnetic sector technology such as the ELEMENT2, with its improved scan speeds, should be considered a viable option to quadrupole technology.

I wish to apologize for any inconvenience caused by these statements.

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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

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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.

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