

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 cup — 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 —

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

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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

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.

Sometimes the rate of ions hitting the detector is too high for the measurement circuitry to handle in an efficient man-

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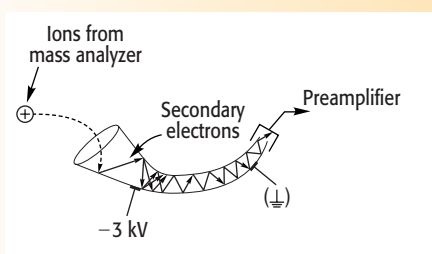


Figure 1. The path of an ion through a channel electron multiplier.

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 10^4 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.

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high-precision isotope ratios using a multicollector detection system.

Discrete dynode electron multiplier. These detectors, which are often called active film multipliers, work in a similar way to the channeltron, but use discrete dynodes to carry out the electron multiplication (2). Figure 2 illustrates the principles of operation of this device. The detector is usually positioned off-axis to minimize the background from stray radiation and neutral species coming from the ion source. When an ion emerges from the quadrupole, it sweeps through a curved path before it strikes the first dynode. On striking the first dynode, it liberates secondary electrons. The electron-optic design of the dynode produces acceleration of these secondary electrons to the next dynode, where they generate more electrons. This process is repeated at each dynode, generating a pulse of electrons that is finally captured by the multiplier collector or anode. Because of the materials used in the discrete dynode detector and the difference in the way electrons are generated, it is typically more sensitive than channeltron technology.

Although most discrete dynode detectors are very similar in the way they work, there are subtle differences in the

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.

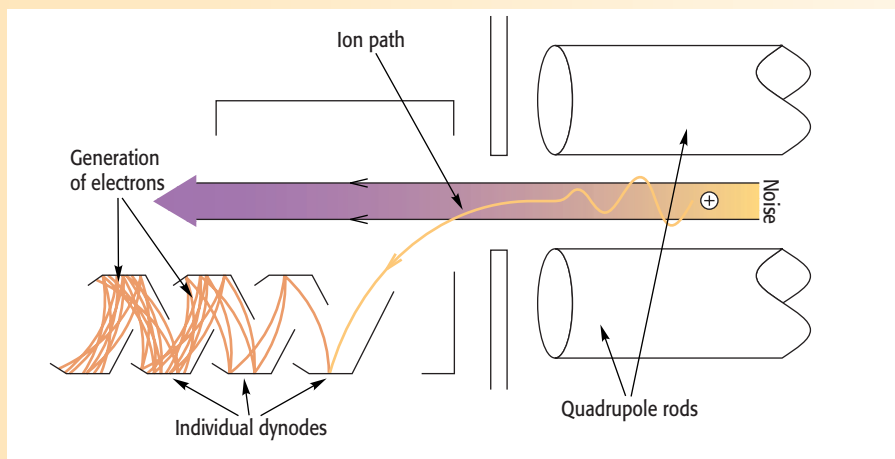


Figure 2 (left). Schematic of a discrete dynode electron multiplier.

trometer 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

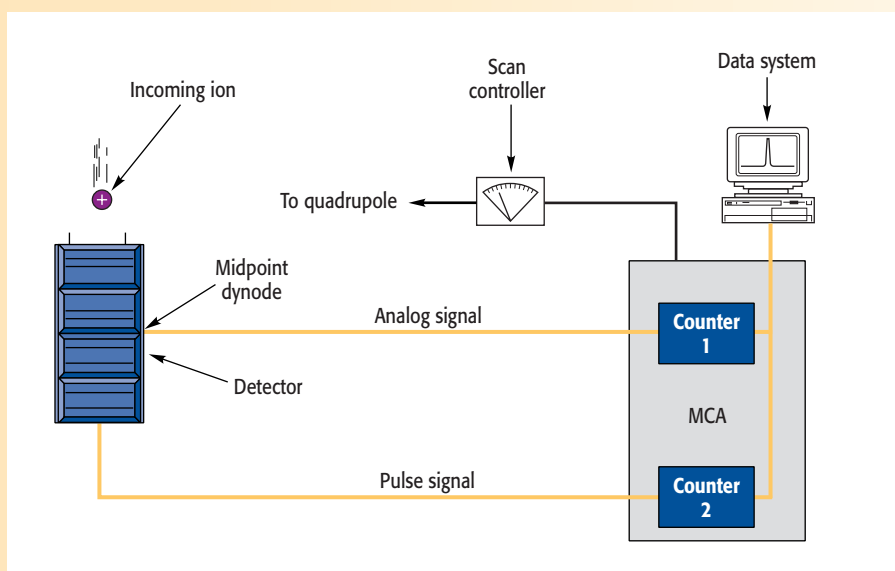


Figure 3 (above). Dual-stage discrete dynode detector measurement circuitry. (Figures 3, 4, and 5 are courtesy of PerkinElmer Instruments, Shelton, CT.)

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 spec-

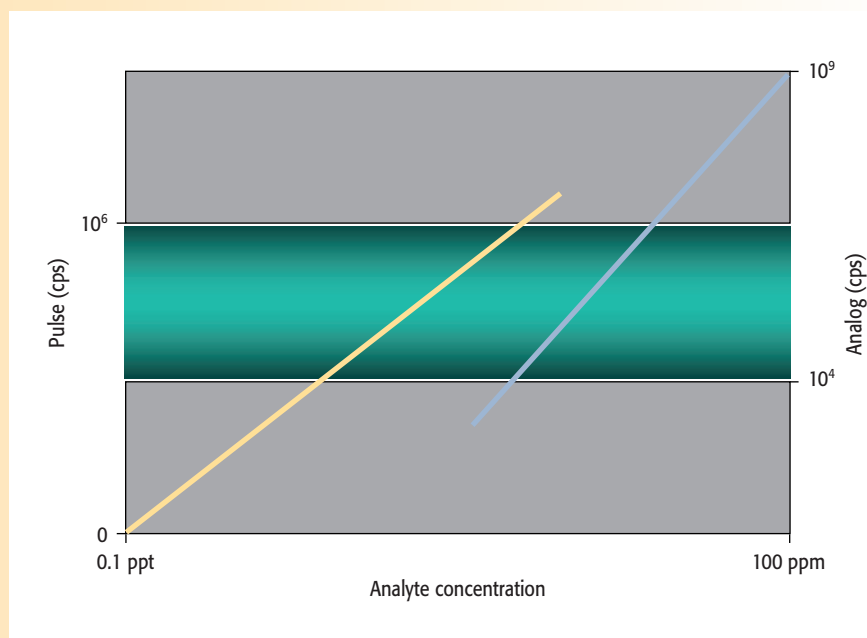


Figure 4. The pulse-counting mode covers rates as high as 10^6 counts/s, and the analog circuitry is suitable from 10^4 to 10^9 counts/s with a dual-mode discrete dynode detector.

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

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.

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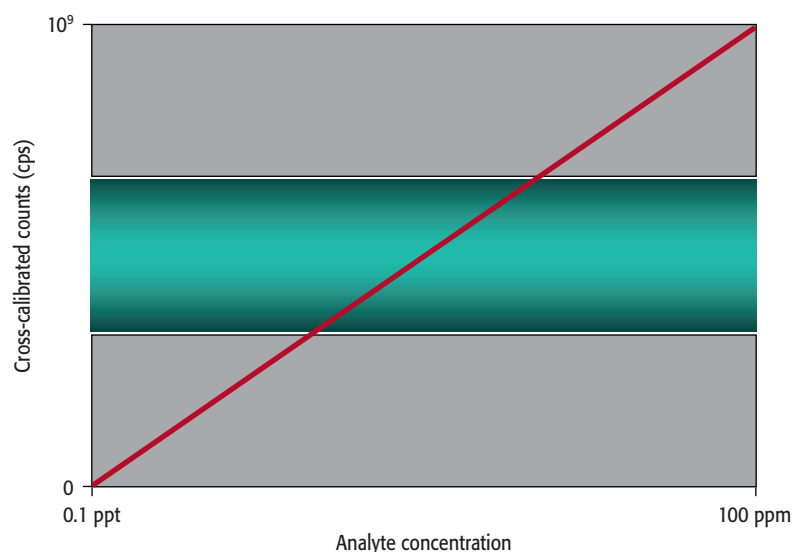


Figure 5. Using cross calibration of the pulse and analog modes, quantitation from sub-part-per-trillion to high parts-per-million levels is possible.