TECHNICAL ARTICLE

Ion Detection in ICP-MS Using Active Film Multipliers

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One of the perennial aims of inductively coupled plasma-mass spectrometer (ICP-MS) development is for higher ion sensitivities and lower detection limits. The electron multiplier ion detector plays a key role in determining the overall detection limits that can be achieved by a mass spectrometer, influencing both the ion sensitivity and the background noise levels.

In developing an ACTIVE FILM Multiplier™ specifically for ICP-MS applications, we concentrated our efforts on maximizing the ion signal count rate, while maintaining a very low background count rate. Te result is an electron multiplier capable of ion detection sensitivities that are greatly improved over channel multiplier technology.

In this presentation, the role and electron multiplier plays in an ICP-MS system discussed. A new type of detector called the ACTIVE FILM Multiplier™ is described, detailing what ACTIVE FILM Multiplier™ are, how they work in detecting ions in a mass spectrometer, and finally, how ACTIVE FILM Multipliers™ perform in an ICP-MS.

ROLE OF THE ELECTRON MULTIPLIER IN AN ICP-MS

Figure 1 shows the functional layout of an ICP-mass spectrometer system. Broadly speaking, the mass spectrometer can be described as having three main sections:

1. The sample introduction system, comprising a liquid sample pumping system that carries the sample to a nebulizer, turning the sample into a fine mist. This mist is then fed into the plasma torch that ionizes the sample producing charged elemental ions. The ions are then introduced into the vacuum system via a set of differentially pumped sampling cones.
2. The quadrupole mass filter separates the ions according to their mass-to-charge ratio.
3. The electron multiplier ion detector detects the ions passed by the quadrupole and produces an amplifying signal that can be processed by the detection electronics before being sent to a computer based data acquisition system.

In order to obtain the highest possible sensitivity from the system, ideally we want the electron multiplier to detect every ion of the selected mass that is passed by the quadrupole mass filter. How efficiently the electron multiplier carries out this task represents a potentially limiting factor on the overall sensitivity of the system. The signal ions exit the quadrupole with a broad spread of exit angles and with kinetic energies up to 25eV. Consequently, the efficient focusing of these ions onto the first dynode of the electron optical design developed for the ACTIVE FILM Multiplier™.

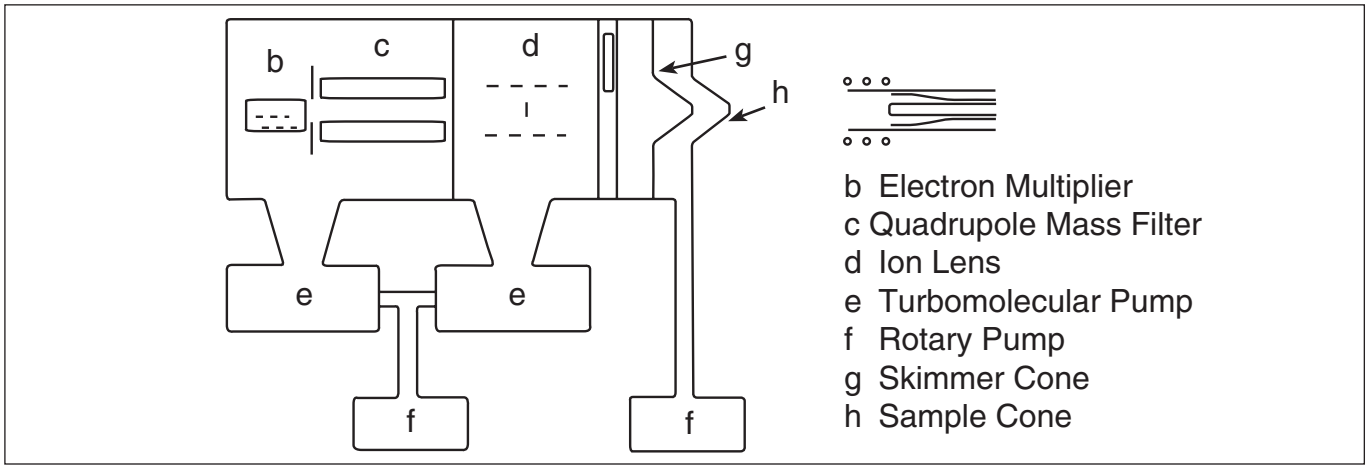

Figure 1. Functional layout of an ICP-MS.

ACTIVE FILM MULTIPLIERS - PRINCIPLES OF OPERATION

ACTIVE FILM Multipliers™ are discrete dynode electron multipliers that use an array of up to 21 electrodes, or dynodes, to carry out the electron multiplication process. The name ACTIVE FILM Multiplier™ is derived from the multi-layer coating that forms the active area of the dynode surfaces where the electron multiplication takes place.

The surface coating used are a new type of extremel stable - in - air material, which is produced using techniques developed for the semiconductor industry. Repeated or long term exposure to air has no effect on the performance of the multiplier.

Figure 2 illustrates the principles of operation of the discrete dynode electron multiplier. First of all, the general arrangement has an off-axis first dynode, requiring the signal ions from the quadrupole to sweep through a curved path before striking the first dynode. This is done to separate the signal ions from the background noise of neutrals and electromagnetic radiation from the ion source, which pass down the axis of the quadrupole and continue on (missing the first dynode of the multiplier) and are not detected. It is essential to remove this background radiation from the signal to obtain a low background count rate, and hence good signal to noise ratios.

When a signal ion strikes the first dynode of the multiplier, it liberates secondary electrons. The electron-optics of the dynode design provides for acceleration of these secondary electrons to the next dynode in the multiplier, where they produce more secondary electrons. This process is repeated at each dynode, generating a growing pulse of electrons that are finally captured by the multiplier collector (or anode). The gain of each dynode depends on the energy of the secondary electrons striking its surface and is controlled by the inter-dynode voltage. Thus, by adjusting the high voltage supply, the multiplier can be set to the required gain.

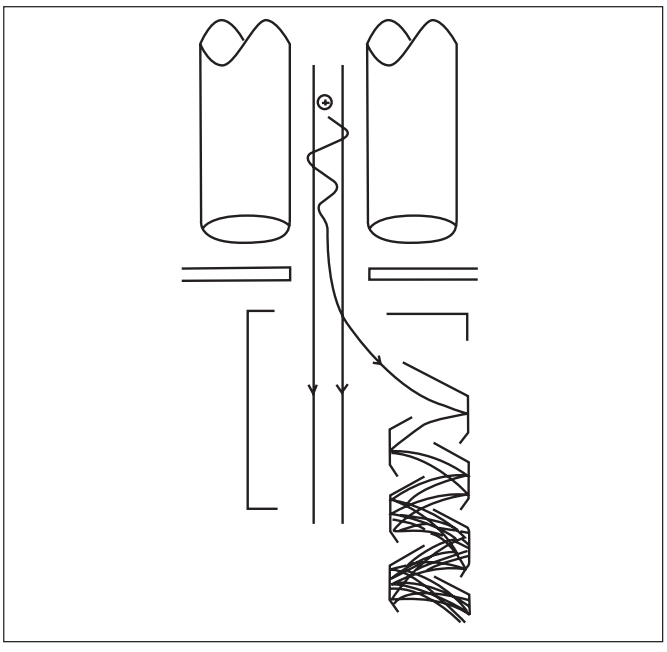

Figure 2. Optics of an Active Film Multiplier for quadrupole applications

A key element in obtaining the highest possible detection efficiency from a multiplier is focusing as near as possible all the ions from the analyzer onto the first dynode. This involves very careful design of the input ion optics of the multiplier. To tackle this problem, highly specialized electron-optical design software was developed, specifically to handle the design of dynodes in an electron multiplier.

Figure 3 is an output plot from the design software and shows the input optics of a 14500 series ACTIVE FILM Multiplier™. The trajectories of ions exiting the quadrupole and being focused onto the first dynode are shown. The dotted lines are euipotential lines spaced at u=intervals of 10% of the high voltage, applied to the first dynode (in this case. HV = 2kV). This pilot clearly shows the very strong lensing effect on the ion trajectories as they pass through the input aperture of the multiplier, bunching the ions together and focusing them onto the first dynode.

Using this kind of plot as a guide, we have been able to produce a design that has a uniformly high ion detection efficiency over the whole area of the multiplier's 11mm diameter aperture. This is demonstrated in figure 4, which shows a three-dimensional plot of the sensitivity (Z axis) of the multiplier over the area of the circular multiplier aperture (X and Y axes). This measurement was taken by scanning the ion beam over the multiplier aperture. This very efficient design of the multiplier input optics is a central element of the higher ion sensitivities that are observed when using this type of multiplier in a mass spectrometer.

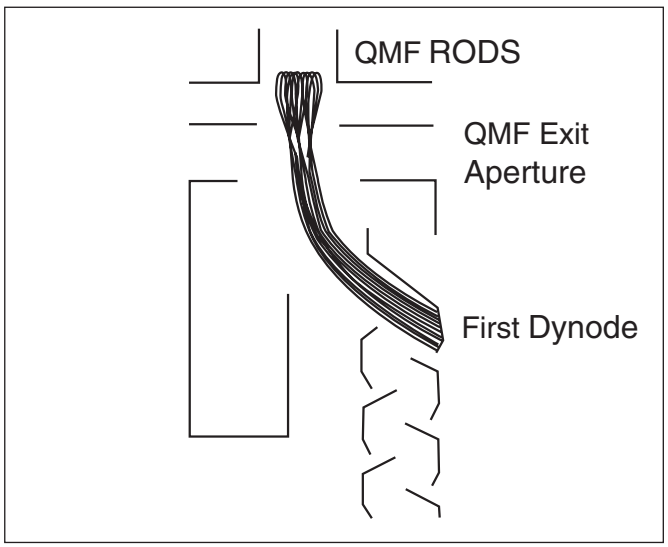

Figure 3. Computer aided design (CAD) model of input ion optics for positive ions exiting the quadrupole mass filter and being focused onto the first dynode

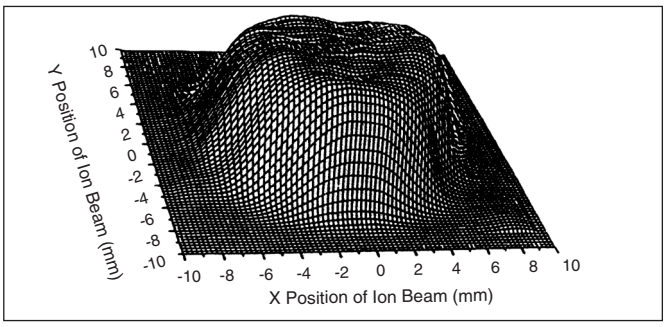

Figure 4. Plot of the sensitivity over the 11mm diameter aperture of a 14500 series Active Film Multiplier.

OPERATIONAL CHARACTERISTICS OF ACTIVE FILM MULTIPLIERS™

In ICP-MS applications, where it is required to be able to detect extremely low ion currents, the electron multiplier is normally operated in pulse-counting mode. In this mode, the ion abundance of a mass peak is determined by counting the output pulses from the multiplier for a fixed time interval, with each output pulse corresponding to a single detection ion. This technique allows signals containing only a few tens of ions to be detected.

The operating gain of a pulse counting ACTIVE FILM Multiplier™ is usually between 106 and 108. Figure 5 shows the Gain vs High Voltage curve for a pulse counting ACTIVE FILM Multiplier™: the initial operating voltage is typically around 2 kV.

The electron pulses output from the multiplier exhibit a distribution of pulse heights that follow a Gaussian like distribution, as shown in Figure 6. The size of the pulse relates to the total amount of charge contained in the pulse. This type of distribution is usually described in terms of the full-width-at-half-maximum, expressed as a percentage of the distribution peak position (FWHM%).

When a multiplier is set to a given gain, say 102, it might be expected that every electron pulse that is output from the multiplier will contain a charge of 106 x e coulombs, where e is the charge on an electron. However, in practice, the charge contained in each pulse output from an electron multiplier varies considerably from pulse to pulse and follows a Gaussian like distribution. The gain at which

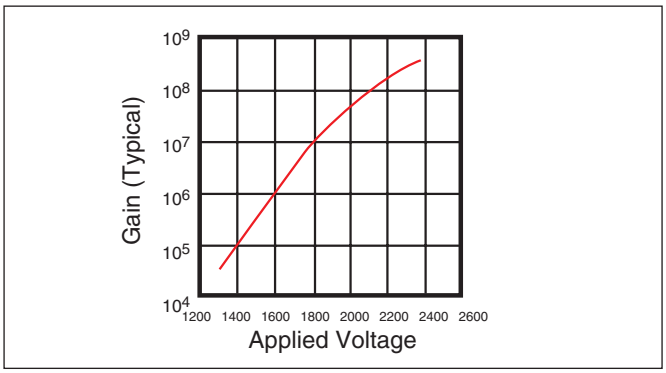

Figure 5. Gain curve for a pulse counting ACTIVE FILM Multiplier™.

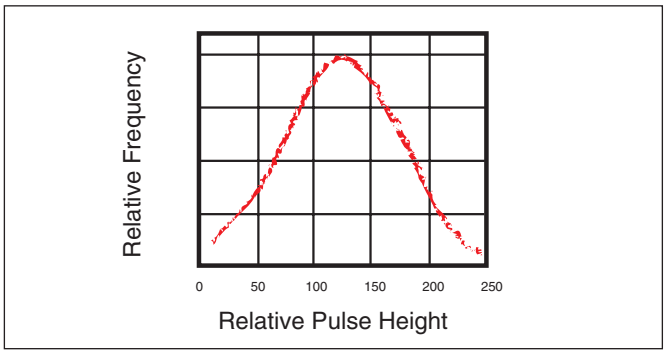

Figure 6. Output Pulse Height distribution of a pulse counting ACTIVE FILM Multiplier™.

the multiplier is set really only refers to the average gain of each pulse. The reason for this variation in the pulse sizes from a multiplier resides in the statistical nature of the secondary electron emission process at each of the dynodes.

The secondary electron yield from each dynode, or dynode gain, is determined by the voltage difference between the dynodes. Figure 7a shows the secondary electron yield from a dynode as a function of the energy of the incident electrons which is set by the inter-dynode voltage. If the voltage of the multiplier was set so that the voltage between each dynode is 150 volts, then the gain of each dynode would be 3.6. This means that, on average, 3.6 electrons are emitted from the dynode surface for each incident electron and the number of secondary electrons emitted for each incident primary electron follows a Poisson distribution shown in Figure 7b. In this case, sometimes two electrons are emitted, and at other times, three or four electrons are emitted. This statistical variation in the secondary electron emission process at each dynode results in the distribution of pulse sizes measured from the output of the multiplier.

The operating voltage of a pulse counting multiplier is usually set by slowly increasing the high voltage until the output count rate reaches a plateau as described in figure 8. This type of curve is seen because the pulse counting electronics connected to the output of the multiplier only counts those pulses larger than a preset discriminator

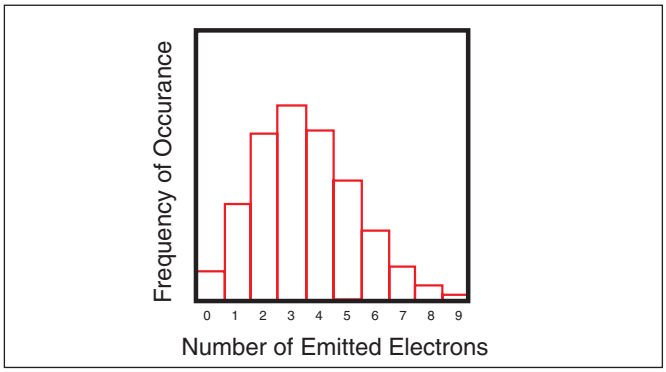

Figure 7a. Dynode gain plotted against incident electron energy.

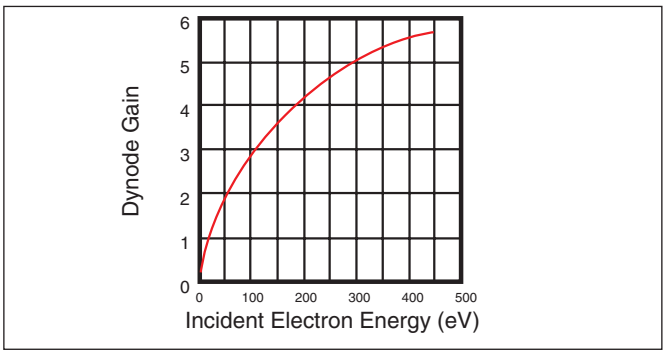

Figure 7b. Probability distribution for th enumber of emitted secondary electrons per incident electron (mean number of electrons emitted = 3.6)

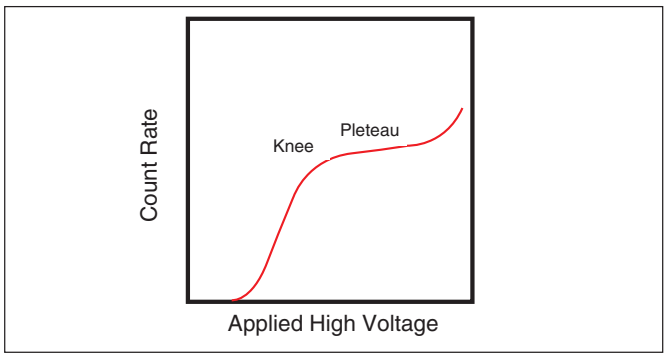

Figure 8. General form of the pleteau curve for a pulse counting ACTIVE FILM Multiplier™.

setting. As the high voltage is increased, the size of the pulses from the multiplier also increases, causing them to cross the discriminator level to be counted and so increase the measured count rate. Eventually, the high voltage is set high enough so that the greater part of the pulse distribution shown in figure 6 is above the discriminator level. At this point, increasing the high voltage is normally set just above the knee on the plateau curve.

To obtain the longest possible life from an electron multiplier, it is important that the applied voltage be kept to the minimum value that achieves the required performance. Operating a multiplier at higher voltages, and hence higher gains, will shorten its operating life.

Standard pulse-counting ACTIVE FILM Multipliers™ will operate linearly to output count rates up to 5 x 106 counts per second. For very high count rates applications, special high count rate models are available that have reduced internal resistance and that will count linearly up to 20 x 106 counts per second.

CONCLUSION PERFORMANCE OF COMMERCIAL ICP-MS INSTRUMENTS

The materials used on the dynode surfaces are very stable. This high stability has two effects on the operation of the multiplier. First the multiplier is stable-in-air, and so repeated or long-term exposure to air has no effect on the performance of the multiplier. Second the multiplier does not require a “burn-in,” as is often the case with channel type detectors.

We conducted sensitivity comparison tests in a number of commercial ICP-MS instruments. In this case of the Perkin Elmer Sciex® ELAN™, 5000 increases in the ion sensitivity obtained when using the ACTIVE FILM Multiplier, over that of the previously installed channel-type detector, were consistently between 30% and 100%, without any significant change in the measured background count rate. This translates directly to an improvement in the instrument signal-to-noise. Tests carried out in several Fisions VG Plasmaquad (Fisions Instruments, Winsford, Cheshire, UK) instruments have resulted in similar sensitivity increases.

Field data from ICP-MS instruments using the ACTIVE FILM Multiplier also indicate that he detector is between 1.5 and 3 times that of the channel-type detector. For example. throughout Australia and Asia, 14 ACTIVE FILM Multiplier's have recently been installed over a period of 18 months in routine environmental and geochemical laboratories as well as in research institutes. Even though some of these laboratories typically replace traditional continuous-dynode detectors every three to four months, none of the Active Film discrete-dynode detectors needed replacing during this period.

The performance characteristics of the ACTIVE FILM Multiplier have led to it attaining wide acceptance in mass spectrometry applications, particularly in applications such as ICP-MS, which are very demanding on the detector used. This has resulted in this type of detector being installed as standard in two commercial ICP-mass specrometers. Active Film Multiplier is also gaining increasing acceptance as a replacement detector in the ICP-MS instruments of several other manufacturers.

ETP electron multipliers

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