

THE ULTIMATE
HANDBOOK FOR

CHANNELTRON® ELECTRON MULTIPLIERS



A Comprehensive Handbook of **CHANNELTRON®**
Electron Multipliers for Mass Spectrometry Applications



CHANNELTRON®

ELECTRON MULTIPLIER

HANDBOOK FOR MASS SPECTROMETRY APPLICATIONS

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PREFACE

Welcome to the Handbook for Channeltron® Channel Electron Multiplier (CEM) Detectors, a comprehensive resource designed to enhance the understanding of the fundamental principles, design specifications, and best practices related to these essential components of mass analysis.

In the following chapters, readers will find a detailed exploration of the construction and operational theory underlying CEMs, as well as insights into their performance characteristics, including detection efficiency and dynamic range. We will also discuss a variety of applications, highlighting the integral role CEMs play in contemporary mass spectrometric instrumentation.

In crafting this handbook, we have focused on providing approachable content, emphasizing information of broad relevance to mass spectrometry practitioners. Each chapter is accompanied by a selection of references for more in-depth study, encouraging readers to delve deeper into specific topics of interest. Although our reference list is not exhaustive, additional resources are provided to facilitate further exploration.

It is our hope that this handbook will serve as a valuable guide for both new users and seasoned professionals, fostering a deeper appreciation and understanding of Channeltron® detectors and their indispensable contribution to the field of mass spectrometry. Thank you for embarking on this journey with us.



CHAPTER 1

INTRODUCTION

HISTORY AND BACKGROUND

Electron multipliers have been used as detectors in mass spectrometers for more than forty years. There are currently two basic types of multipliers in use: the first include the copper-beryllium (CuBe), discrete dynode multipliers, which are the oldest and which trace their roots to photomultiplier tube technology. These detectors have the advantage of being able to produce high output currents (in excess of 100mA), but suffer from the disadvantage of being relatively unstable when repeatedly exposed to atmosphere. In recent years, new structures have been fabricated based on aluminum dynodes, which are reportedly less susceptible to degradation but are bulky and relatively expensive.

The second type of multiplier is the continuous dynode multiplier. The vast majority of these are fabricated of glass, although some are constructed from coated ceramic materials or are a combination of glass and ceramic. These detectors are, in general, much more suitable for applications requiring frequent exposure to atmosphere. Most of these detectors are of the single channel type; however, microchannel plates¹ (two dimensional arrays of single channels) have been used in applications involving simultaneous imaging of an entire mass spectrum and Time-of-Flight Mass Spectrometry.

Channeltron[®] Single Channel Electron Multipliers (CEMs) are durable and efficient detectors of positive and negative ions as well as electrons and photons. Figure 1-1 illustrates the basic structure and operation of the Channeltron[®] CEM. A glass tube having an inner diameter of approximately 1mm and an outer diameter of 2, 3, or 6mm is constructed from a specially formulated lead silicate glass. When appropriately processed, this glass exhibits the properties of electrical conductivity and secondary emission. Today, CEMs are the most widely used detector in quadrupole and ion trap mass spectrometers and find many applications in magnetic sector instruments as well.

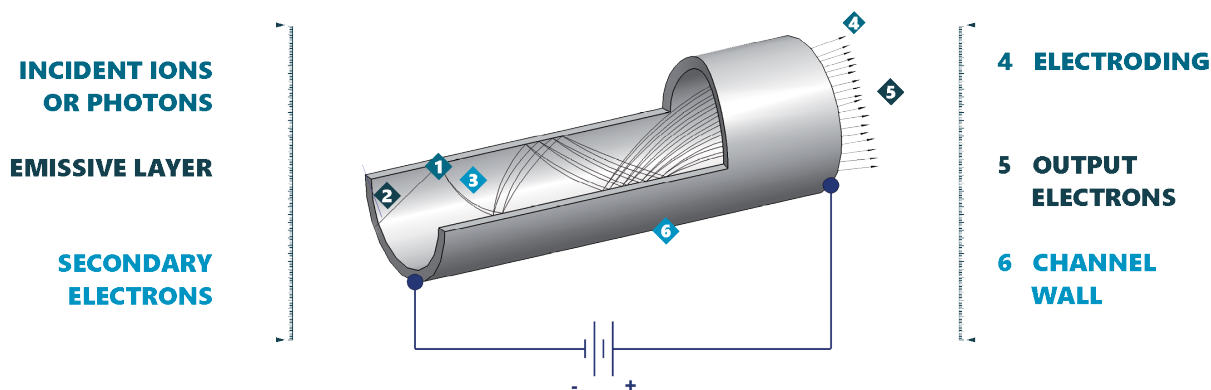


Figure 1-1 Cutaway View of a CEM

EARLY DEVELOPMENTS

The idea for an electron multiplier based on an integrated device combining secondary emission and a resistive chain dates from 1930²; however, it was not until suitable materials became available - based largely on work by Blodgett³ - that operational devices became a reality. The first successful multipliers were fabricated in 1958 by Goodrich and Wiley⁴, then with Bendix Research Labs. These were followed closely by similar developments at Mullard Research Labs and the Laboratoires d'Electronique et de Physique Appliquee (L.E.P.) in Europe⁵.

The Channeltron® Channel Electron Multiplier, a major technological advancement in electron detection and amplification, was introduced by the Electro-Optics Division of Bendix Corporation in the U.S. The term "Channeltron®" was patented in 1964, marking the inception of a legacy in high-performance electron multiplier technology. In 1973, the Electro-Optics division underwent a management-led leveraged buyout and rebranded itself as Galileo Electro-Optics Corporation operating under this name until 1999 when BURLE INDUSTRIES, INC. acquired Galileo's Scientific Detector Products group. The acquisition led to the establishment of Burle Electro-Optics, Inc. as a wholly owned subsidiary.

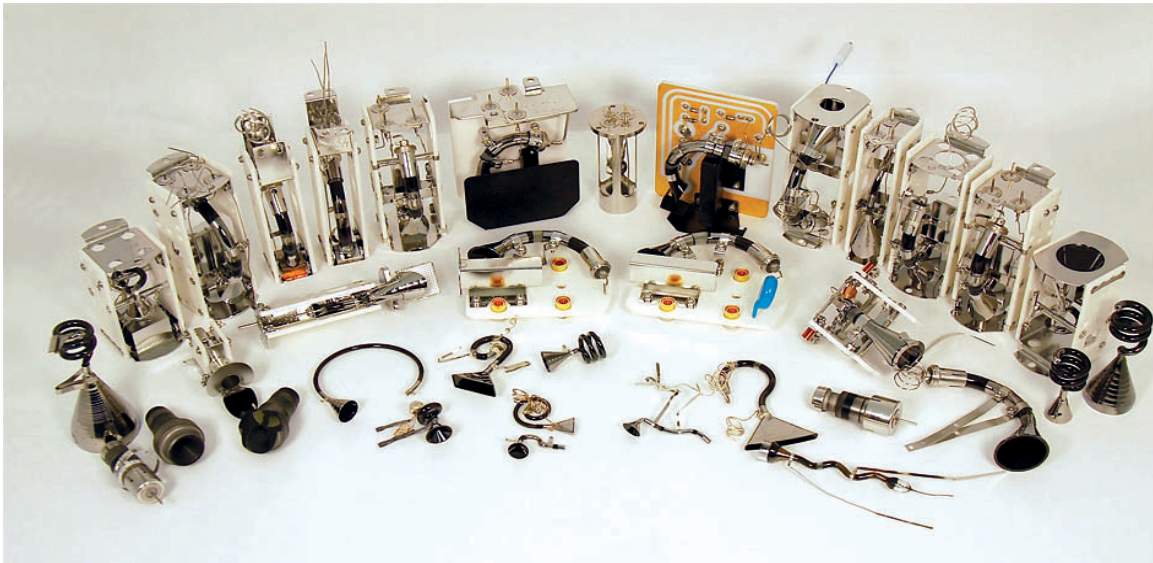


Fig. 1-2 *The Wide Variety of Channeltrons® Available*

The evolution of the Channeltron® continued with its acquisition by the Photonis Group in 2005, which led to the rebranding of Burle as Photonis USA. This acquisition combined operations at sites in Lancaster, Pennsylvania, and Sturbridge, Massachusetts. In 2018, the Photonis Group strategically split Photonis USA Pennsylvania into two distinct entities, naming them Photonis Defense (PA) and Photonis Scientific, Inc. (MA), to better cater to their respective markets. The year 2023 marked another transformation for the company, with Photonis's parent organization rebranding itself to Exosens, aligning its vision toward leading advancements in detection and

imaging technologies. Despite this rebranding, the legal identities of the previously existing companies remain intact, ensuring that Channeltron® continues to be manufactured under the Photonis brand, now part of Exosens.

Early devices were designed primarily for operation in the pulse counting mode for space science applications. Their small size and low power requirements made them ideal detectors for planetary atmospheric research and solar system exploration. By the mid 1970s, the Channeltron® garnered significant interest for use in laboratory analytical instruments, particularly mass spectrometers. Their durable glass surfaces could endure repeated cycling between vacuum and atmosphere without the performance degradation typically seen in CuBe discrete dynode multipliers. New CEM designs were developed using materials capable of handling the higher bias currents required for efficient analog operation. As a result, the Channeltron® CEM has established itself as a leading detector for quadrupole mass spectrometers.

RECENT INNOVATIONS

Recent developments in Channeltron® CEM technology have extended the dynamic range (Photonis' exclusive EDR option), improved detection efficiency at higher masses, and enhanced lifetime under the less than ideal environments typically encountered in mass spectrometers. Improvements in conversion dynode technology have resulted in structures capable of operation at higher voltages and materials with improved ion-to-electron conversion yields for better sensitivity at higher masses. Finally, the use of the Spiraltron™ technology in CEM configurations (as in the Magnum™ Electron Multiplier, see Figure 1-3) coupled with improved materials and processing has the potential to significantly enhance the lifetime of current detectors over those manufactured in the early days of the industry.



Fig. 1-3 *Magnum Electron Multiplier*

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CHAPTER 2

FABRICATION AND OPERATION OF CHANNELTRON® CEMs

CEM STRUCTURE AND FABRICATION

Channeltron® CEMs are constructed from a specially formulated lead silicate glass developed and produced at Photonis Scientific, Inc. Glass billets or boules (illustrated in Figure 2-1) are extruded into tubes having an inner diameter of 1mm and outer diameters of 2, 3, or 6 mm. As noted below, the I.D. is an important consideration for CEM operating parameters. The O.D. of detectors is more a matter of historical development.



Fig. 2-1 Glass Billet

Early multipliers produced by Bendix and Galileo were used primarily in space applications where weight and power consumption were strictly controlled. The 2 mm devices proved most suitable for these applications when properly mounted and cushioned against the force of rocket launches. Devices developed for laboratory mass spectrometry needed to be more rugged to withstand handling by operators and also have greater surface area to dissipate joule heating due to higher currents produced in analog CEMs. The 6mm tubes have proven very effective in this regard and are the most popular size in use today. The 3mm devices are gaining in popularity since they can significantly reduce the size of the detector, be fabricated in a wider variety of shapes and also have been found to withstand the higher currents required for analog operation. They are also a good compromise between small size and ruggedness.



Fig. 2-3 CEM Fabrication Steps

The extruded tubes are cut into lengths of approximately 5" and a circular, conical aperture is produced on one end by forming the glass over a hot carbon tool. In cases where a rectangular aperture is desired, additional forming is done. The tube is then curved or formed to the desired shape (see section on Operation) and the cone is ground to its final dimensions. The output end of the CEM is ground and polished to prevent chipping of the glass. The formed glass then undergoes various cleaning and processing operations including a treatment in high purity hydrogen at high temperature. The reduction of lead oxide on the glass surface after the hydrogen treatment turns the glass a shiny black color. This process produces the conductivity and secondary emissive characteristics critical to CEM performance. The conductive coating is interrupted at one point on the outer surface to produce a single series conduction path down the interior of the multiplier. After this, thin film metal electrodes are deposited via thermal evaporation. These fabrication stages are illustrated in Figure 2-3 for a typical 4770-type channel. The finished multiplier is then ready to be assembled into a ceramic and stainless steel housing.

THEORY OF OPERATION

Figure 2-4 illustrates the basic operation of a CEM. An ion strikes the input face of the device typically produces 2-3 secondary electrons. These electrons are accelerated down the channel by a positive bias. The electrons strike the channel walls, producing additional electrons (and so on) until, at the output end a pulse of 10⁷ to 10⁸ electrons emerges. For positive ions, the input is generally at a negative potential of 1200 to 3000 volts and the output is at ground. For detection of negative ions, the input is generally at ground or some positive potential and the output is at a high positive voltage. This, of course, requires some form of decoupling in order to handle the high voltage signal. Some methods for accomplishing this will be discussed in Chapter 3.

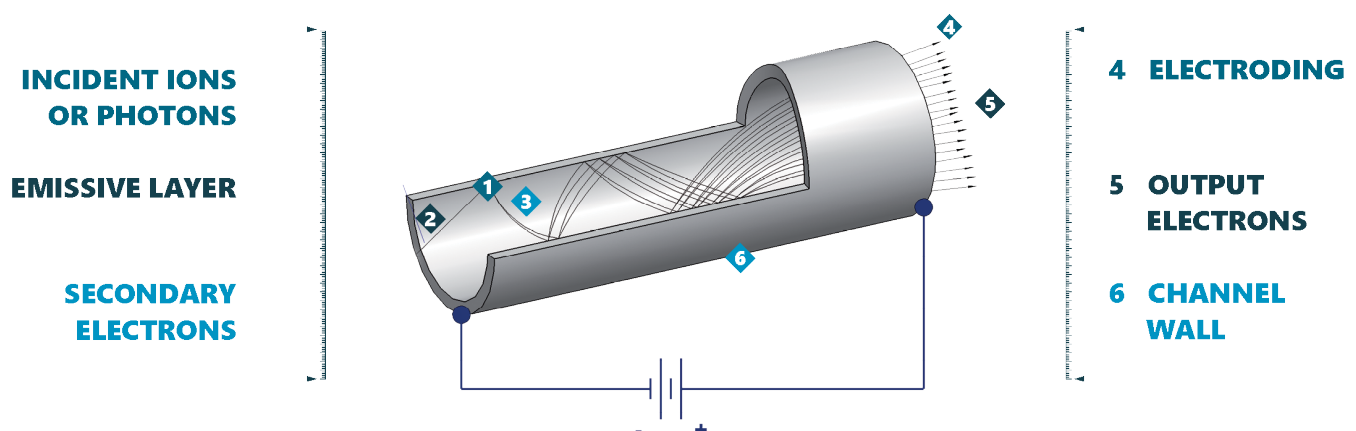


Fig. 2-4 Basic Operation

OPERATIONAL PARAMETERS

Material properties, processing, and physical geometry can all play an important role in the performance of a Channeltron® CEM. Figure 2-5 shows a cross-sectional view of the active surface

of a CEM. Secondary emission takes place within the first 200Å of the surface. Underneath this is a conductive layer several hundred to several thousand angstroms thick. The following are some of the more important parameters to consider when using CEMs in mass spectrometry applications:

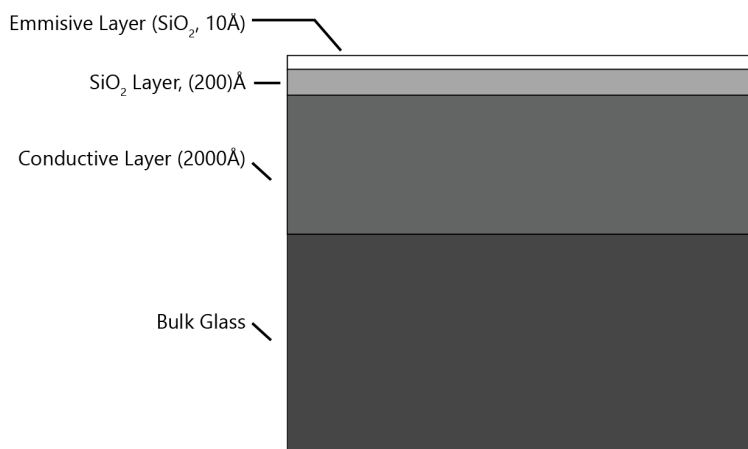


Fig. 2-5 Cross-Sectional View Surface Structure of CEMs

The gain of a CEM is defined as the ratio of the output current to the input current (I_o/I_i). Gain is, in general, a function of the secondary emission coefficient (δ) of the glass, the applied voltage (V_{cem}), and the length-to-diameter ratio (l/d) of the tube¹. Figure 2-6 shows a typical gain vs voltage curve for a CEM. As the voltage applied to the CEM is increased, a point is reached where space charge saturation occurs. This happens when secondary emission approaches unity due to positive wall charging at the output end of the channel. At this point, the gain vs voltage characteristic becomes highly non-linear. The desired operating point on the curve is determined primarily by whether the CEM is to be operated in the analog or pulse counting mode (ref. Chapter 3).

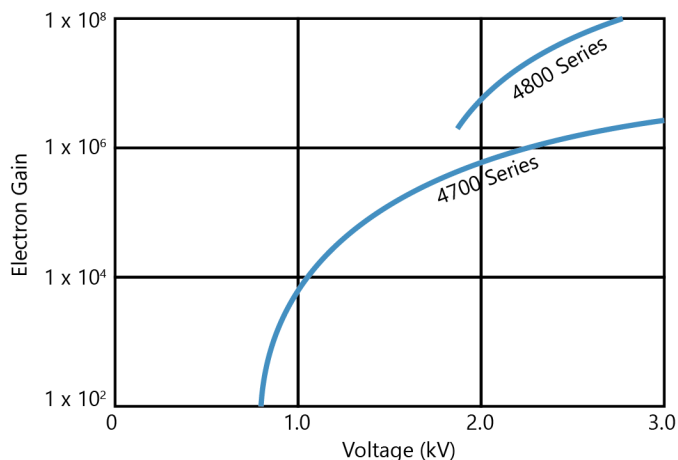


Fig. 2-6 Typical Gain Characteristics (4700 and 4800 Series)

Early in the development of CEMs, it was discovered that gains in excess of about 10^4 to 10^5 could not be sustained in straight channel geometry devices². This is due to the high electron

densities existing within the channel near the output end. Gasses adsorbed on the surface of the walls are desorbed and ionized, forming positive ions. These ions travel back toward the input of the device. When they strike the walls near the input, they produce secondary electrons which are subsequently amplified and detected at the output end as a noise pulse (i.e. not due to an incident particle, but generated within the CEM itself). This phenomenon is known as ion feedback. Curving the channel effectively minimizes this problem by preventing desorbed ions from traveling far enough to gain sufficient energy to produce secondary electrons. This enables devices to be constructed which produce analog gains of 10^7 or more and saturated (pulse counting) gains in excess of 10^8 .

PULSE HEIGHT DISTRIBUTION (PHD)

PHD is the distribution of the amplitude of CEM output pulses. A typical PHD can be obtained by feeding the CEM pulses into a device called a multi-channel analyzer (MCA). The MCA assigns a value to each pulse based on its amplitude and also counts and displays the number of pulses recorded at each value. CEMs designed for analog operation generally produce a negative exponential PHD curve (see Figure 2-7). Pulse counting CEMs produce a quasiguassian PHD (see Figure 2-8) because, in space charge saturation, the output pulses are all very nearly the same amplitude. A figure of merit for the PHD of a pulse counting CEM is the full-width-at-half-maximum (FWHM). This is usually expressed as a percentage and is calculated as follows:

$$\text{FWHM} = (G_0/rG) \times 100\%$$

Where G_0 is the modal (peak) gain and rG is the width of the PHD at half the peak value. The narrower the PHD, the smaller the FWHM, with all output pulses approaching the same value. Typical pulse counting CEMs yield a FWHM on the order of $< 75\%$ down to some as low as 20% . In general, the larger the length-to-diameter ratio of the device, the narrower the PHD.

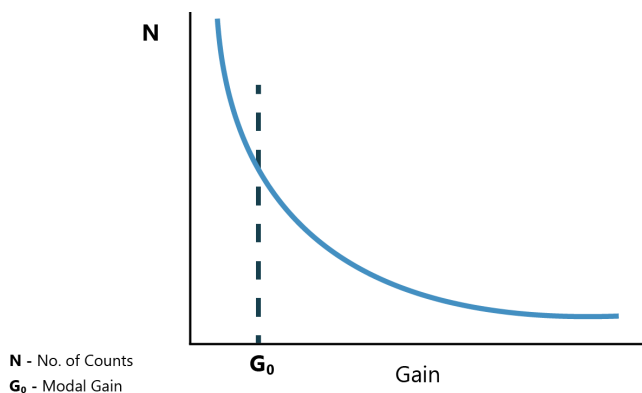


Fig. 2-7 Analog Pulse Height Distribution (PHD)

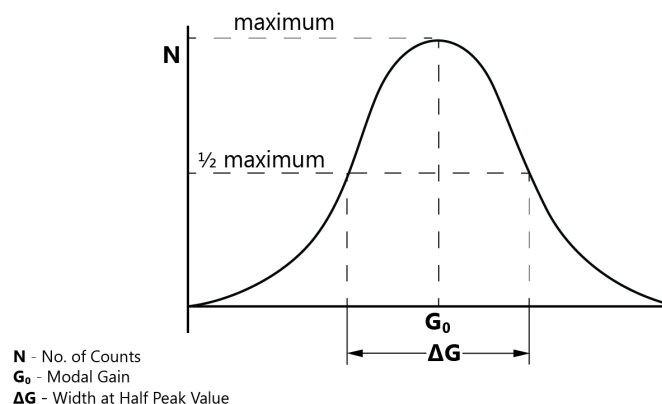


Fig. 2-8 Pulse Counting Pulse Height Distribution

DYNAMIC RANGE

Dynamic range can have several definitions depending upon application; however, it is usually defined as the ratio of maximum to minimum detectable signal. For CEMs, dynamic range is a measure of maximum count rate capability in the pulse counting mode or maximum linear output current in the analog mode. Both of these are dependent upon the CEM bias current at the operating voltage point.

Analog CEMs will produce a linear output up to a value equal to approximately 10-20% of the bias current. This is limited because the bias current supplies the electrons necessary to sustain the secondary emission process as noted above. For example, standard 4700 Series Channeltron® CEMs generally have bias currents on the order of 30-40mA. This means that the maximum linear output can be on the order of 5-10mA. Figure 2-9 illustrates typical linearity of a standard 4700 Series multiplier as a function of input current.

The maximum count rate capability of a pulse counting CEM is dependent not only on bias current, but also on channel capacitance as well as the condition of the channel surface. As the count rate is increased beyond a certain point, the pulse amplitudes begin to decrease and eventually fall to a level below the discriminator threshold. The upper limit on count rate is determined by the output pulse width which, for standard CEMs, is about 10-20 ns. Figure 2-10 is a plot of CEM gain versus output count rate for a typical 4800 Series multiplier.

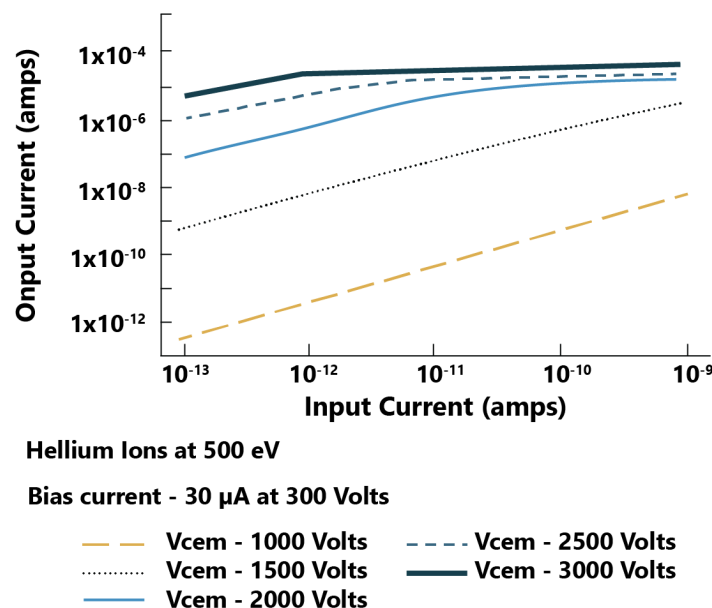


Fig. 2-9 Typical Linearity 4700 Series Channeltron®

DETECTION EFFICIENCY

Detection efficiency is the probability of a charged particle (or photon) incident on the CEM input producing an output pulse. This parameter is strongly dependent upon the energy, mass and velocity of the incident particle as well as the number of charges on the particle and the angle of incidence.^{3,4,5} For mass spectrometry applications, the most important particles of interest are positive and negative ions. Electron detection efficiency is important in some instances, such as when a conversion dynode is being used and the CEM is detecting secondary electrons emitted from the dynode surface. Photon detection can also be important in a negative sense in that it is often a source of unwanted noise. Figures 2-11, 2-12, and 2-13A & B show graphs of typical detection efficiencies as a function of energy for electrons, ions and photons respectively. The case of ions is unique; the detection efficiency is a function of both ion energy or, more properly, ion velocity at the point of impact on the secondary emitting surface and ion mass to charge ratio (m/z). Thus, for efficient ion detection of increasing mass, the velocity of the impacting ion must be increased concurrently—usually by increasing the ion energy. Figure 2-14 shows a graph of CEM response versus m/z ratio. Methods for enhancing ion detection efficiency, especially at higher masses, as well as minimizing photon noise will be discussed in Chapter 3.

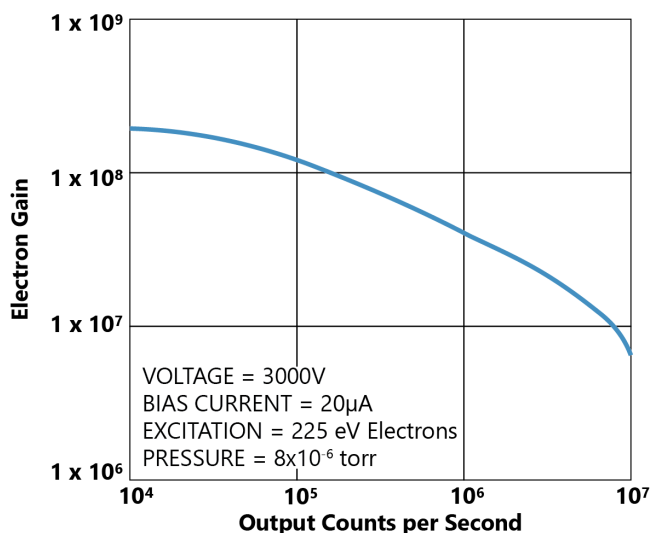


Fig. 2-10 Typical Electron Gain vs. Count Rate 4800 Series Channeltron®

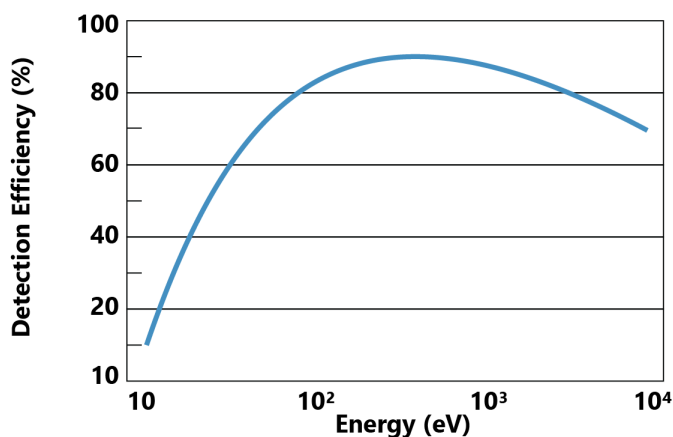


Fig. 2-11 Electron Detection Efficiency

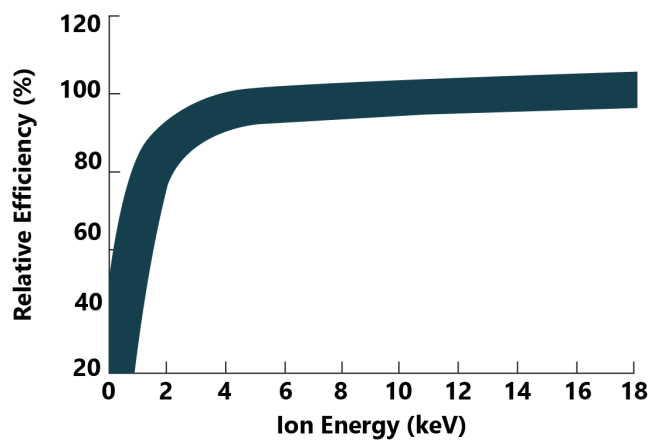


Fig. 2-12 Relative Ion Detection Efficiency

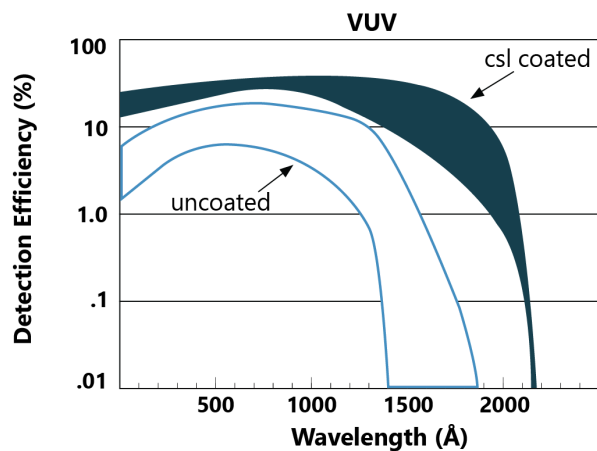


Fig. 2-13A Photon Detection Efficiencies

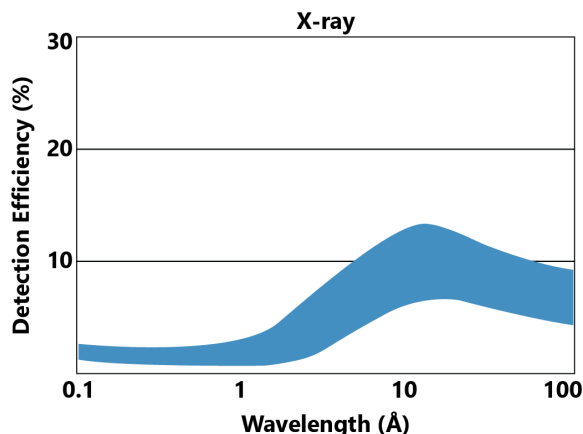


Fig. 2-13B Photon Detection Efficiencies

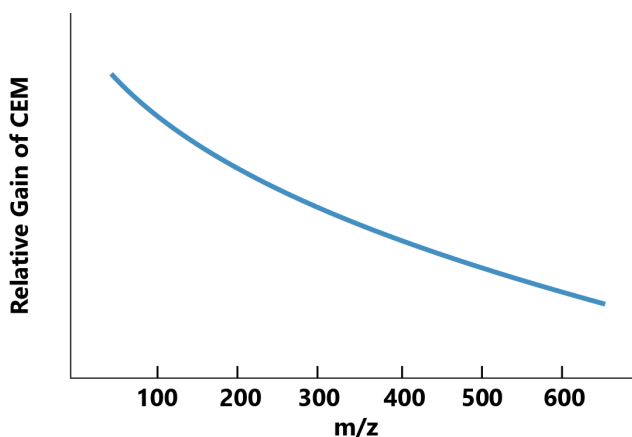


Fig. 2-14 Relative Ion Detection Efficiency

DARK NOISE

Dark noise is defined as the output current or count rate from the CEM when no input signal is present. One of the major features of the Channeltron[®] CEM is its extremely low dark noise characteristic. This enables very low signal levels to be detected—especially in the pulse counting mode. A distinction must be made between “dark current” and “dark count rate.” Dark count rate is a pulse counting parameter and is generally on the order of .05 count per second or less for most CEMs. Dark current, on the other hand, is a DC phenomenon and can be affected by conditions outside the CEM—such as leakage in the collector assembly, etc. Proper design of an analog detector should result in dark currents of $<< 1$ pA @ 3kV and typical Channeltron[®] CEM dark currents may be as low as 10-15 μ A.

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CHAPTER 3

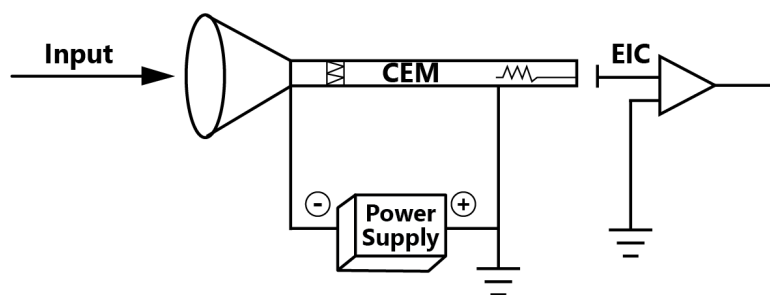
CHANNELTRON® CEM APPLICATIONS INFORMATION

MODES OF OPERATION

Channeltron® CEMs used in mass spectrometry applications may be operated in either the analog or pulse counting mode. By far, the majority are operated in the analog mode— especially where there is sufficient sample to produce relatively high signal levels. In some applications, however, where extremely small amount of sample are available, pulse counting CEMs capable of counting up to 108 counts per second are available.

ANALOG MODE

Any CEM may be operated in the analog, or current measurement, mode. Many early models, however, suffered from limited dynamic range when used in this manner. As noted in Chapter 2, the linearity of the CEM in the analog mode is strongly dependent upon the conductivity (bias current capability) of the device. For this reason, new materials were developed which yielded an order of magnitude higher conductivity than early 4000 Series multipliers. To further enhance linearity, a high conductivity option is also available. These characteristics are incorporated into the popular 4700 Series Channeltron®. Analog CEMs have an electrical isolated collector (EIC) and an internal bias resistor (described below) which allow linear output currents of up to 10-50mA. Figure 3-1 shows a schematic of a typical analog application for detecting positive ions. Negative ion detection in the analog mode is complicated by the fact that the signal must generally be collected at a high positive potential. Some possible approaches to this problem will be discussed later in this Chapter.



Positive Ion Detection

Fig. 3-1 Typical 4700 Series Connection for Positive Ion Detection

PULSE COUNTING MODE

The primary difference between CEMs operating in the pulse counting versus the analog mode is that pulse counting CEMS produce output pulses with a characteristic amplitude whereas analog CEMs have a very wide distribution of out put pulse amplitudes (refer to Figures 2-7 and

2-8). This is because pulse counting CEMs operate in space charge saturation as explained in Chapter 2. All early CEMs were designed primarily for pulse counting operation; however, the dynamic range of these devices was limited to about 10⁶ counts per second maximum. The new materials developed for use in the 4700 Series detectors proved effective in increasing the performance capabilities of pulse counting CEMs as well. 4800 Series devices can be operated in excess of 10⁸ counts per second. Figure 3-2 compares the count rate performance capability of 4000 and 4800 Series multipliers. The high, saturated gain of pulse counting multipliers allows one to set a discriminator level to reject low-level noise while passing all the signal pulses. This results in very good signal-to-noise performance. Figure 3-3 shows schematics of typical pulse counting-hook-ups. An additional advantage of the pulse counting mode is that, for negative ion detection, the signal can be capacitively decoupled from the high voltage DC inside the vacuum chamber.

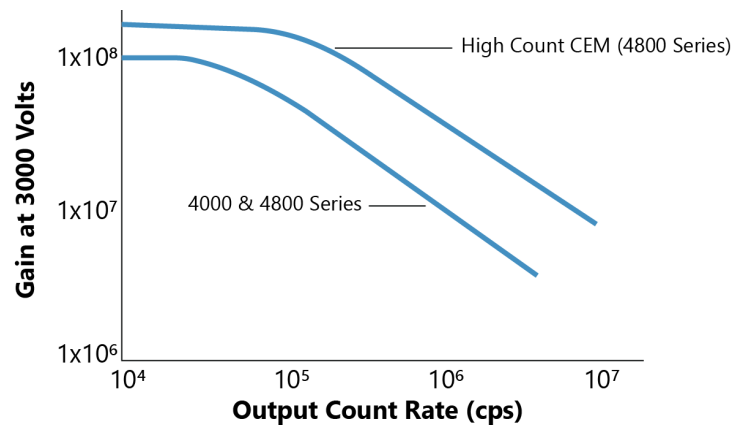


Fig. 3-2 Comparison of 4000/4200 Series & 4800 Series Count Rate Capability

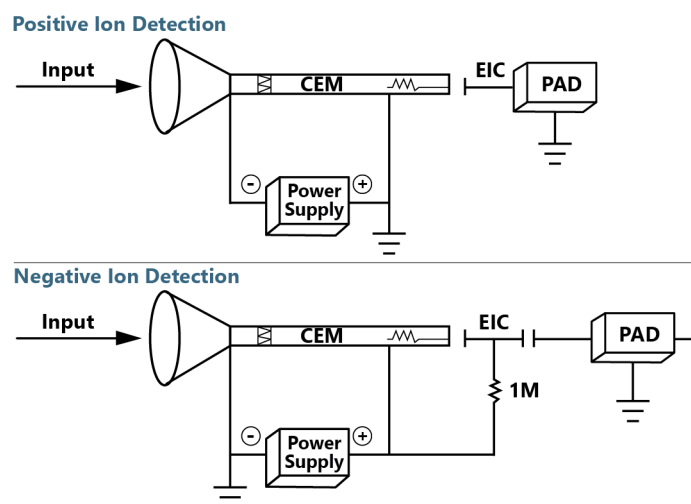


Fig. 3-3 Typical 4800 Series Connections

The 4800 Series multipliers may be operated in either the pulse counting or the analog mode simply by changing the gain of the CEM. Analog operation is accomplished by lowering the voltage to a level where the output pulses are not saturated. The 4800 Series CEMs have slightly lower performance than 4700 Series detectors for analog operation however, due to their higher resistance (lower bias current). In order to produce the high gain required for pulse counting operation, the channel length-to-diameter ratio must be $>50:1$ whereas for analog operation the l/d needs to be only approximately $30-35:1$. A longer channel results in a higher channel resistance and lower bias current for a given voltage.

At very high count rates, the performance of pulse counting CEMs is limited by the pulse width of the output pulses. If input events occur at rates in excess of about 107, it is possible that several events may occur within the time required for a single CEM output pulse and therefore some may be lost.

INTERNAL BIAS RESISTOR

For proper operation, the CEM must be maintained at a positive bias. This means that the collector must be the most positive element in the detector circuit. In the early days of CEMs, this was accomplished via an external bias arrangement as shown in Figure 3-4. This is still the case with most 4000 Series multipliers which have electrically isolated collectors. Because the outside of the channel as well as the inside can be made resistive, the collector bias resistor can be integrated into the body of the CEM

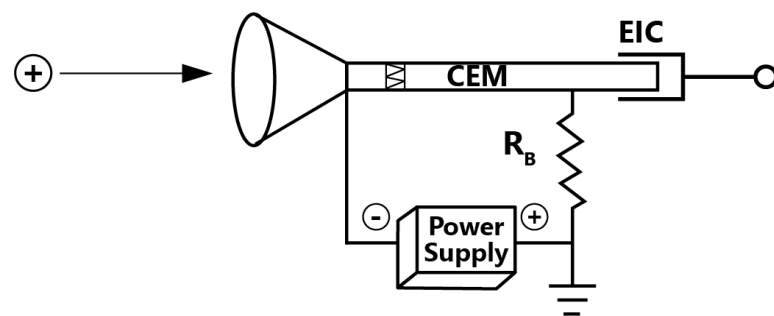


Fig. 3-4 External Bias Resistor

itself, thus simplifying circuitry and reducing installation time. This is accomplished by appropriate electroding of the tube as shown in Figure 3-10. The CEM bias current is allowed to flow on the outside of the CEM body, through the bias resistor to the grounded output connection (for positive ion detection). This biasing arrangement is currently standard on all 4700, 4800, and 4900 Series Channeltron® CEMs.

The optimum value depends on the overall CEM resistance which can have a fairly wide change over different units of the same model. Also, as the CEM ages and higher voltage is applied, a higher voltage is consequently applied across the CEM-collector gap. This potential difference can have an effect on gain and other operational parameters, and it would be best if a constant potential could be maintained. Zener diodes are also used to "clamp" the bias voltage in place of the bias resistor (see Figure 3-6).



Fig. 3-5 Integral CEM Bias Resistor

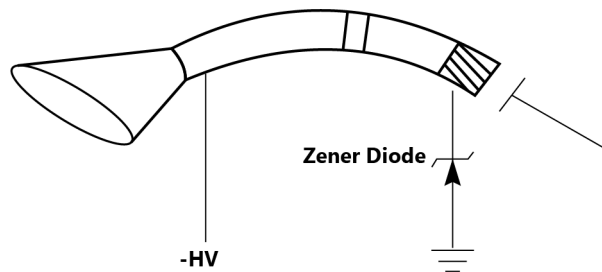


Fig. 3-6 Zener Diode Biasing of CEM

OPERATING POINT

For optimum lifetime, the CEM should always be operated at the minimum voltage required for acceptable performance. Increasing the voltage beyond this point will not improve performance significantly and only serves to reduce the life of the detector. The actual operating point is, in part, determined by the mode of operation.

ANALOG OPERATING POINT

Many commercial mass spectrometers in use today employ autotune programs which set the multiplier voltage based on noise and sensitivity measurements. Sometimes a CEM with very high gain will have difficulty tuning properly because at a voltage high enough to yield sufficient detection efficiency, the signal may be saturated. This can usually be overcome by preconditioning the CEM. This is accomplished by operating the CEM at some set voltage with an input signal for a short period in order to degas the device.² Most multipliers used in mass spectrometry applications today are preconditioned at the factory. In addition, most manufacturers' autotune programs allow for smaller bias voltage increments which in turn allow more precise determination of the best operating point. Figure 3-7 illustrates the "clean-up" phase of CEM operation.

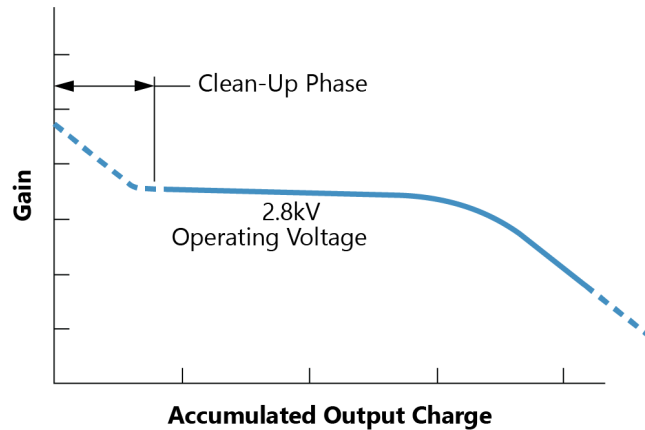


Fig. 3-7 CEM Clean-Up Phase (Pre-Conditioning)

The actual operating point is determined when the multiplier voltage is high enough to provide sufficient gain and at the same time provide sufficient accelerating potential to the ions to insure acceptable detection efficiency (sensitivity).

PULSE COUNTING OPERATING POINT

The operating point for a CEM in the pulse counting mode is usually determined by the point at which a plateau is reached in the count rate versus voltage characteristic. A typical curve is illustrated in Figure 3-9. The plateau occurs when all the signal is being collected at the input of the CEM. Additional increases in voltage raise the gain, but the count rate remains essentially constant. Eventually, a point is reached where ion feedback (refer to Chapter 2) becomes significant due to the very high gain, and the count rate again increases rapidly. This is an undesirable condition since the extra counts are produced within the CEM itself and are not the result of an input.

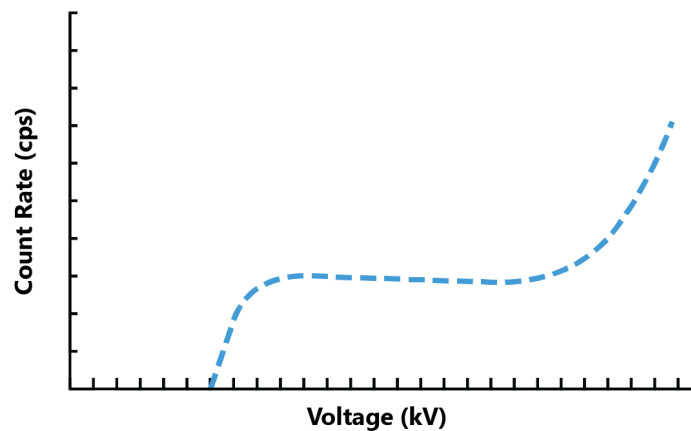


Figure 3-8 Count Rate vs. Voltage

The optimum operating point is about 50-100 volts beyond the "knee" of the curve in Figure 3-14. As the multiplier ages, the knee moves to the right and the voltage must be increased. Typ-

ical lifetime characteristics under ideal conditions are illustrated in Figure 3-20 for either analog or pulse counting operation.

HIGH MASS DETECTION

The operating point for a CEM in the pulse counting mode is usually determined by the point at which a plateau is reached in the count rate versus voltage characteristic. A typical curve is illustrated in Figure 3-9. The plateau occurs when all the signal is being collected at the input of the CEM. Additional increases in voltage raise the gain, but the count rate remains essentially constant. Eventually, a point is reached where ion feedback (refer to Chapter 2) becomes significant due to the very high gain, and the count rate again increases rapidly. This is an undesirable condition since the extra counts are produced within the CEM itself and are not the result of an input.

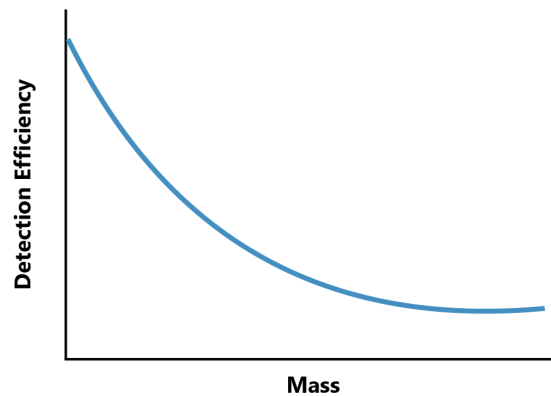


Figure 3-9A Relative Efficiency vs. Mass

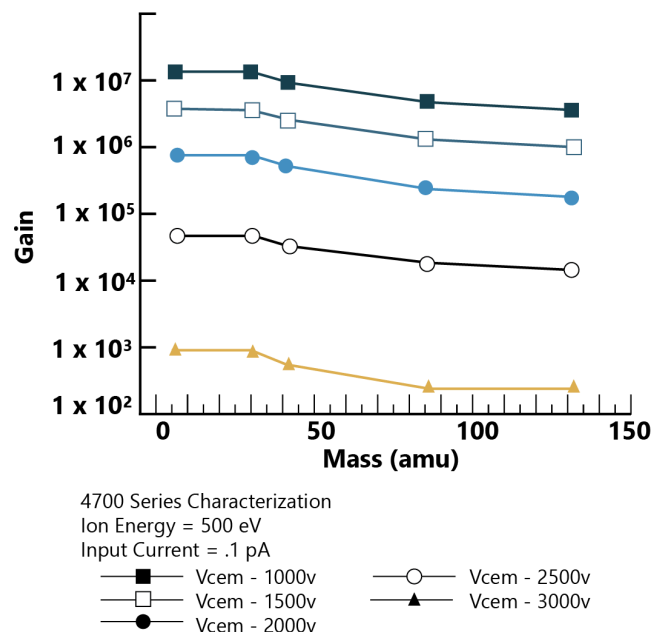
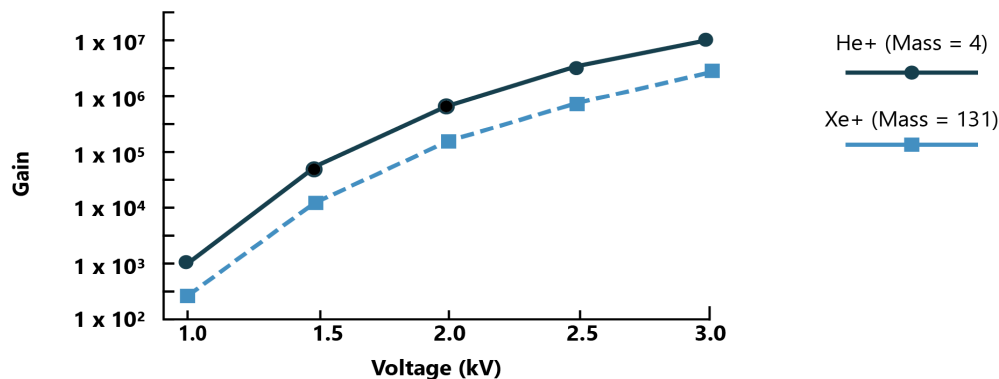


Figure 3-9B Gain vs. Mass



4700 Series CEM Characterization
 Ion Energy = 500 eV
 Input Current = .1 pA

Figure 3-9C Gain vs. Voltage

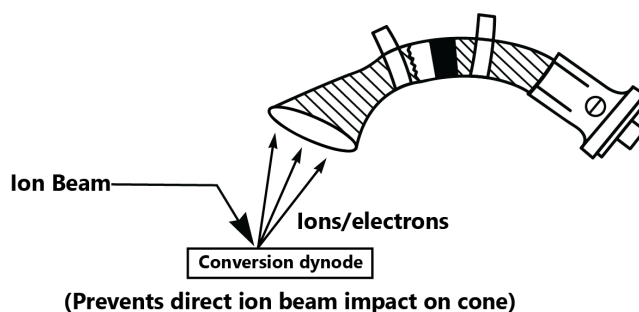


Figure 3-10 Conversion Dynode

CONVERSION DYNODES

Perhaps the most popular means of enhancing detector sensitivity at higher masses is to use a conversion dynode. A conversion dynode is simply a separate surface (usually a metal) which can be held at a high voltage (e.g. 3 to 20kV or more). The dynode potential serves to accelerate the ions to a point where good conversion efficiency (to either electrons or secondary ions) occurs. The CEM is then used to detect the emission from the dynode surface. Figure 3-11 illustrates this concept schematically.

The operation of conversion dynodes has been widely discussed in the literature.^{3,4,5} Usually, they are used in the detection of positive ions and the conversion products are thought to be electrons and lower mass ions. The high negative potential on the dynode then serves to direct electrons toward the CEM input which is held at a somewhat lower negative potential. For the detection of negative ions, the situation is somewhat different. A high positive potential on the conversion dynode will not result in many secondary electrons being collected by the CEM since the dynode will tend to recapture electrons. One way around this is to float the CEM at still a higher potential in order to collect the secondary electrons. This is most easily accomplished if pulse counting operation is used since the high voltage signal can be capacitively decoupled with little difficulty. Another method which has been described and used for a number of years

is to make use of the fact that, in addition to electrons, positive ions are also produced at the surface of the conversion dynode.⁶

The positive dynode potential guides the secondary ions into the CEM input which is maintained at a negative potential, allowing the signal to be collected at ground for the case of positive primary ion detection. Experimental evidence indicates that above approximately 10,000 daltons, the majority of the conversion products are secondary ions with very few electrons produced.⁷ It is recommended to maintain a potential difference of over 3kV between the CEM and the conversion dynode for effective detection of positive secondary ions. If, for example, the dynode and the CEM input are at virtually the same voltage, the ion beam will not be deflected at all—neither into the dynode surface nor into the CEM input. As the dynode becomes more negative than the CEM, positive ions are deflected toward the dynode, striking the surface and producing secondary particles. For the conditions where the CEM is more negative than the dynode (or the dynode is “off”), the ions are deflected directly toward the CEM. It has been found that a grid over the surface of the CEM input can significantly enhance EM performance with this type of conversion dynode. This is because the grid prevents particles generated in the cone from escaping and also inhibits particles generated at the dynode surface from being accelerated past the cone where they would not be detected.

LIFETIME CONSIDERATIONS

The lifetime of a CEM can be significantly affected by the environment in which it is operated. There are essentially two areas of the detector which are susceptible to degradation in performance; the output and the input areas of the inner channel wall.

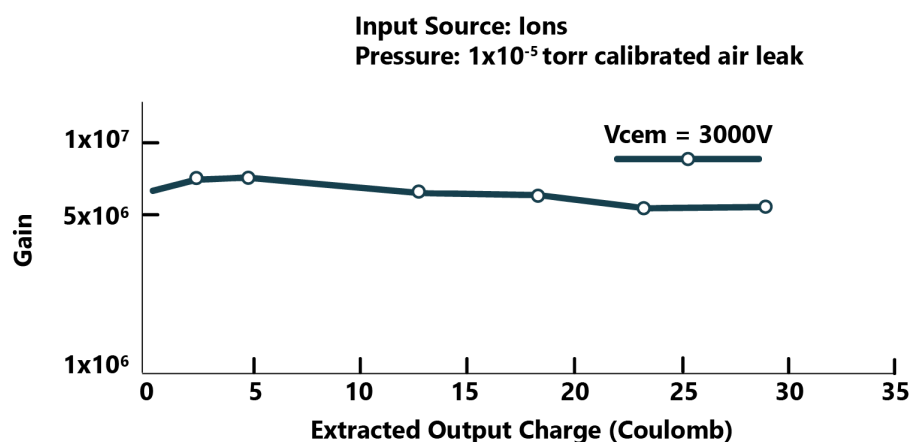


Figure 3-11 Typical Gain

OUTPUT SURFACE DEGRADATION

The high density electron cloud at the output end of a CEM can cause physical and chemical changes to the surface, which can reduce the secondary emission coefficient of the glass. This, in turn, causes a reduction in gain. Under very clean, ultra-high vacuum (UHV) conditions, the normal life of the output surface (measured in terms of total output charge) is on the order of thirty coulombs or more. Figure 3-13 shows gain as a function of total output charge for a typical CEM under these conditions. Considering the environment in many mass spectrometers, it is clear that higher pressures, temperatures, and exposure to generally hostile substances may have a significant impact on multiplier lifetime.

CEM lifetime will vary as a function of specific application and environment, but is typically on the order of about one year at 40 hours operation per week.

INPUT SURFACE DEGRADATION

In Mass Spectrometry applications, the channel input area of CEMs is an significantly affects its lifetime. The impact of high molecular weight ions at high energies can result in chemical changes in the glass surface and even physical sputtering which can reduce the effective sensitivity of the device. Some users have even established that a CEM with decreased sensitivity can sometimes be “rejuvenated” by changing the location of impact of the ion beam on the CEM cone. This can be accomplished using a small magnet or, in some cases, by rotating the CEM with respect to the input beam.

LIFETIME OPERATION

Various methods to improve the lifetime of CEMs in mass spectrometers are being explored. One means of improving output lifetime is to increase the channel output surface area. This may be accomplished by using a microchannel plate which has many thousands of channels per millimeter of active area. A somewhat less drastic approach is to use a Spiraltron™ CEM configuration. The spiral section consists of six single channels which are twisted-barber pole fashion - around a solid center. This results in effectively six times the output surface area and, in addition, allows a straight channel geometry since the curving to prevent ion feedback is done internally. Photonis' Magnum family of electron multipliers (5900 series) uses this technology to dramatically increase detector life and dynamic range.

Lifetime of the input surface may be optimized by using a conversion dynode (see previous

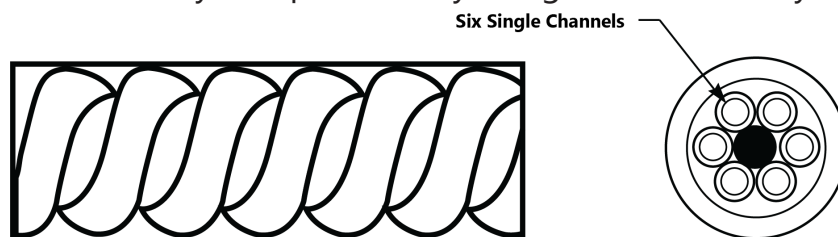


Figure 3-12 Exosens' Magnum™ Multiplier Utilizing Exclusive Spiraltron™ Technology

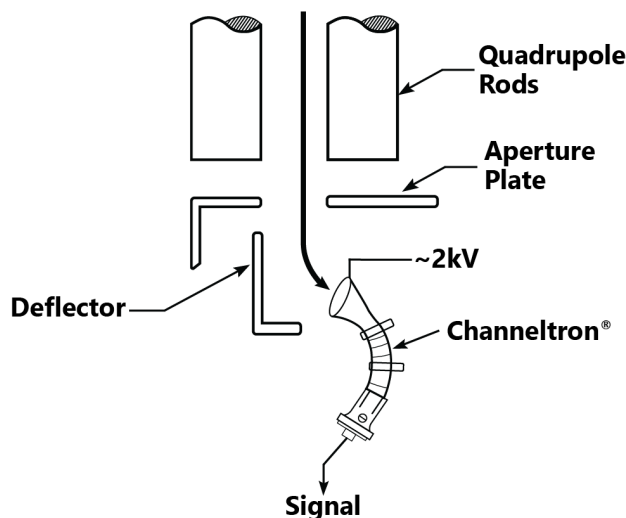
section). When configured to detect secondary electrons, this prevents ions from striking the CEM directly. The CEM surface is much less affected by electrons than by much more massive and chemically active ions, in addition, positive secondary ions from the conversion dynode are less likely to be deleterious to the CEM surface since they are usually gas and oxide ions and not heavy organic molecular ions.

ION OPTICS OF CEM DETECTORS

The interface between a detector and any type mass analyzer is of great importance in both instrument and detector design. Most CEMs shipped from the manufacturer are housed in a ceramic and stainless steel enclosure designed to optimize detector performance. Such factors as geometry, proximity and potential of other electrodes, and grids may all have a significant impact on sensitivity and dynamic range of the detector. Modern ion optics modeling tools such as SIMION10 have greatly facilitated the design of detectors for mass spectrometry.

QUADRUPOLE INSTRUMENTS

The straight line geometry of most quadrupole mass analyzers generally necessitates mounting the detector off-axis to avoid noise caused by neutrals and/or photons from the filament or due to the decay of metastables within the analyzer or detector chamber. A typical geometry is illustrated in Figure 3-15. The CEM Input aperture is located out of the line-of-sight of the analyzer exit aperture. This effectively eliminates detection of neutrals and photons generated



by the filament or in the analyzer housing since they travel in a straight line through the detector housing. Of greater consequence in GC/MS applications are photons generated due to the decay of helium metastables within the detector chamber itself. These tend to be scattered in all directions and can be detected if they impinge upon the multiplier input.

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HANDLING, STORAGE, AND INSTALLATION OF CHANNELTRON[®] ELECTRON MULTIPLIERS

Channeltron[®] CEMs are rugged and reliable detectors. By following a few simple procedures as outlined in this chapter, one can obtain maximum life and optimum performance from the detector.

HANDLING CEMs

The active surface of a Channeltron[®] CEM may be repeatedly exposed to atmosphere without degradation of its detection characteristics. When handling the multiplier, however, it is necessary to use clean, talc free gloves or finger cots to prevent contamination by oils which may severely degrade performance. Lint, dust, or loose particles may be removed using high purity dry nitrogen gas.

In cases of severe contamination, such as oil backstreaming or vacuum failure, the CEM may be cleaned via the following procedure:

1. Immerse the device in electronic grade or higher purity in Isopropyl alcohol and stir for five minutes using a magnetic stir plate.
2. Ultrasonic treatment in Isopropyl alcohol for five minutes.
3. Repeat steps 1 and 2 as necessary using fresh solvent.
4. Remove the CEM from the solvent and blow dry using dry, oil-free nitrogen.
5. Heat the detector in an oven at approximately 80°C for at least fifteen minutes.
6. Blow dry the detector using dry, oil-free nitrogen and install.

WARNING

Isopropyl Alcohol is a highly flammable liquid and should be used with caution

Note: Cleaning CEMs in this manner may temporarily increase the gain of the device. This is due to desorption of surface materials and is generally short-lived.

CAUTION

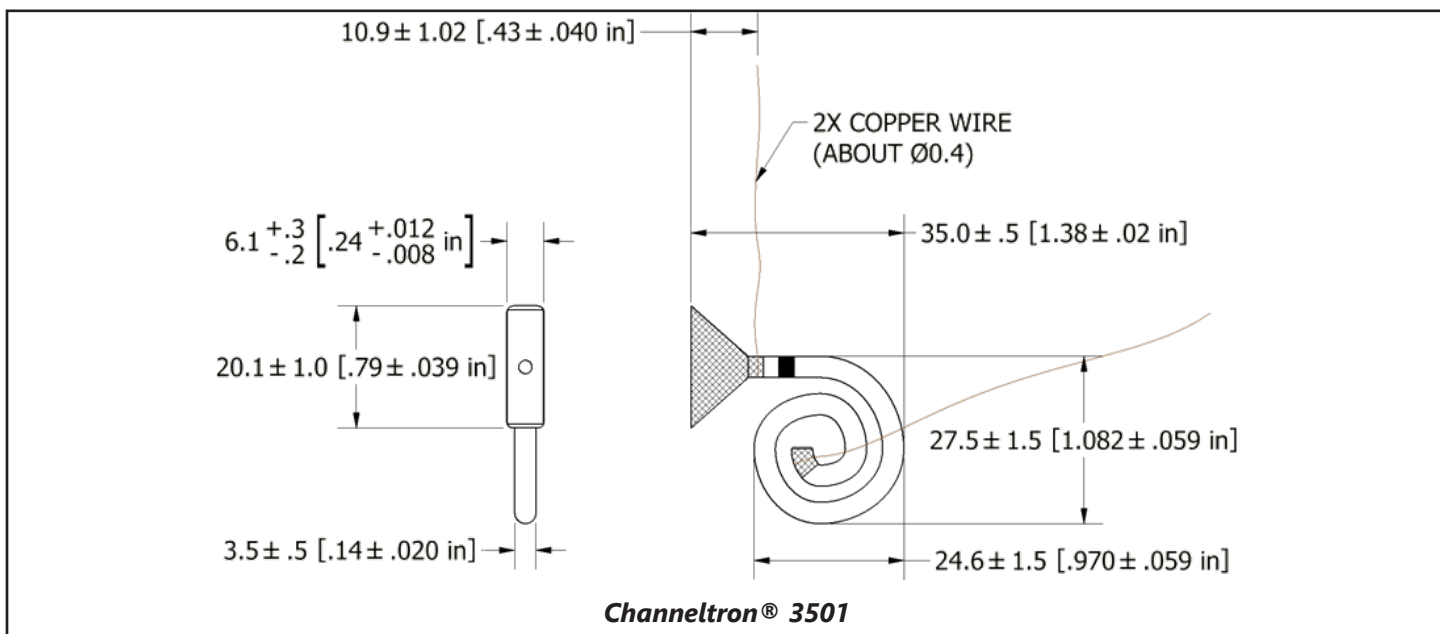
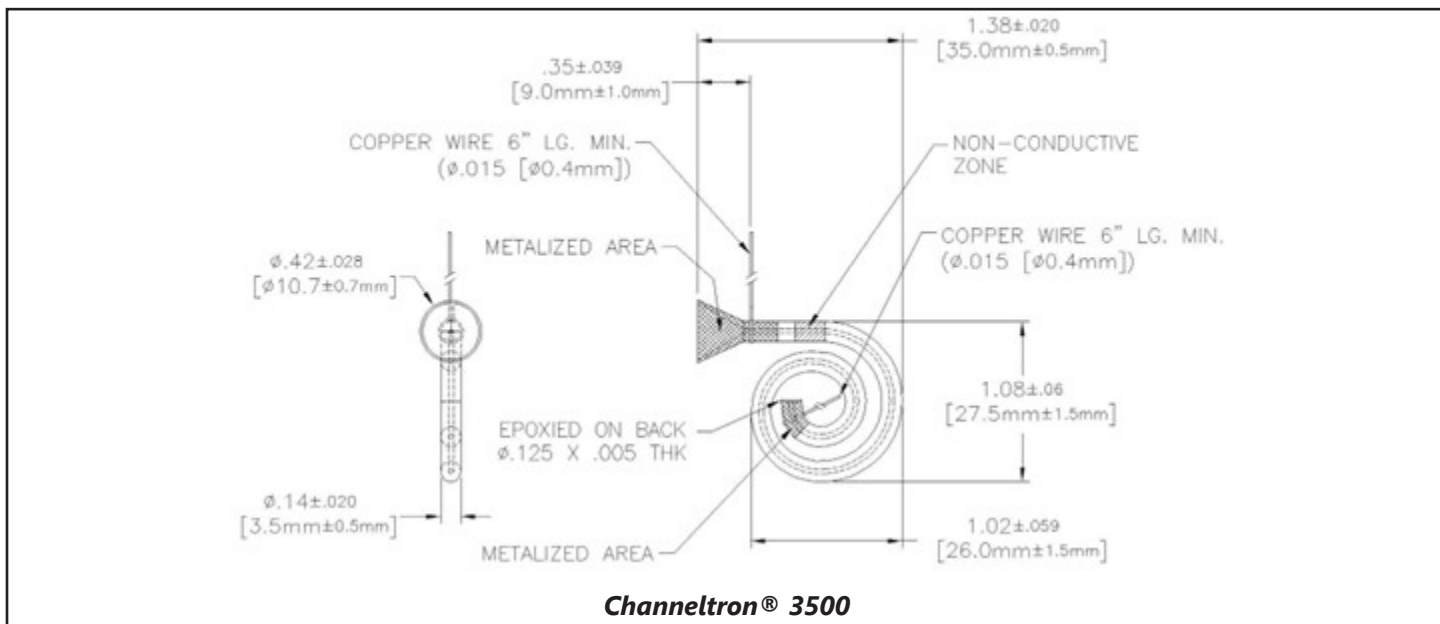
Never operate a CEM which has been contaminated by oil or other gross contaminant. To do so may destroy the device or, at the very minimum, result in serious degradation of performance.

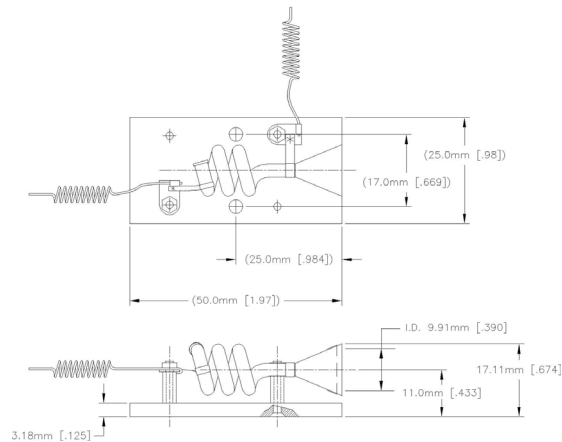
STORAGE OF CEMs

Channeltron® CEMs may be stored for up to one year in their original packaging. For longer periods, the user should consider storage in a dry nitrogen box or under a vacuum of 10⁻² torr or better. Humid or “dirty” environments should be avoided. High humidity may cause the CEM resistance to increase somewhat. In most cases, this is not detrimental to the performance of the device.

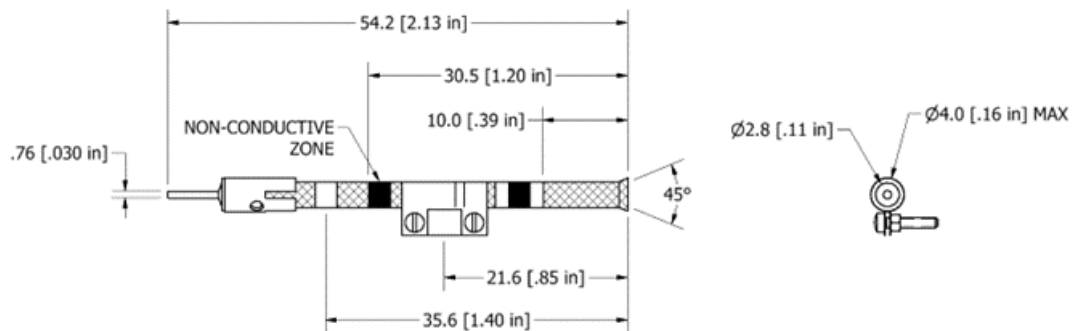
DIMENSIONAL DATA

The CEM drawings in this section represent only a small number of Photonis' standard detector assemblies from each series of multipliers. All dimensional data is subject to change without notice. For complete, up to date, dimensional data drawings on a specific multiplier model(s), please contact our Sales Dept. at 1-800-648-1800 or 508-347-4000 (in MA).

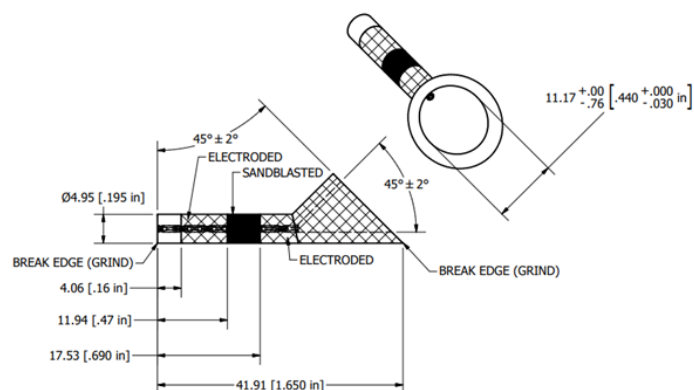




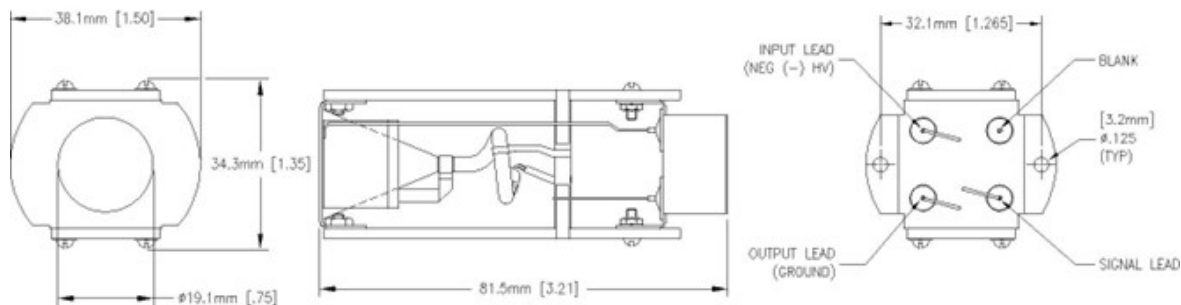
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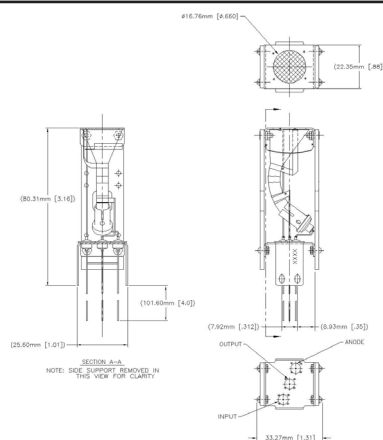
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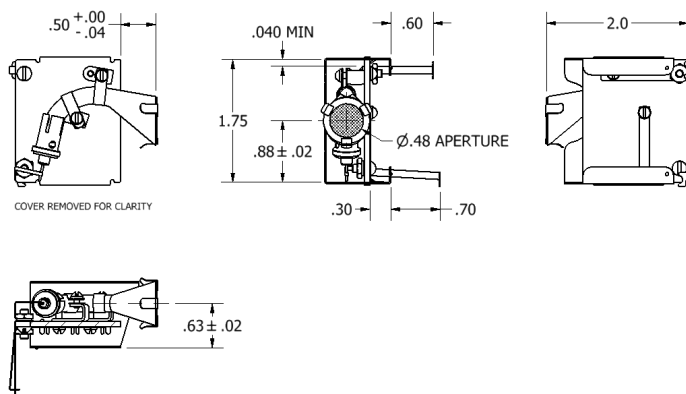
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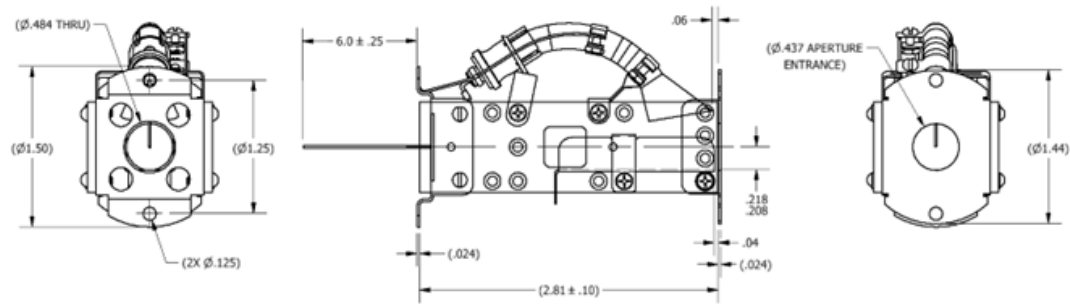
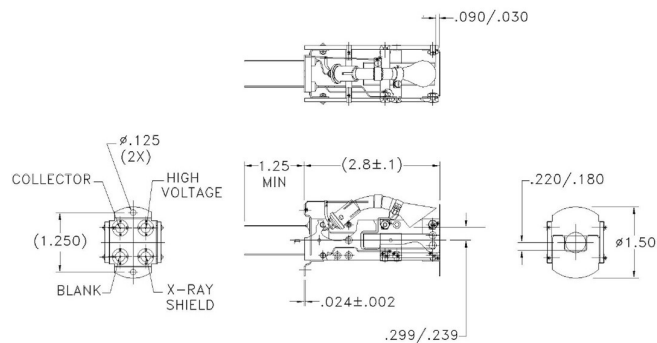
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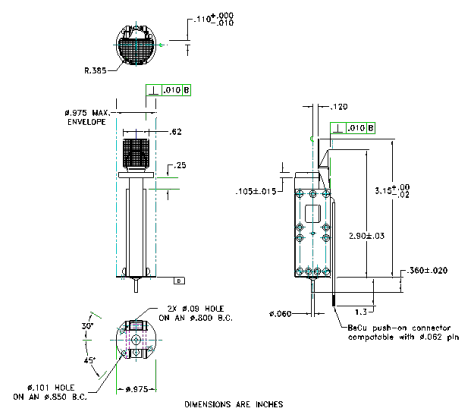
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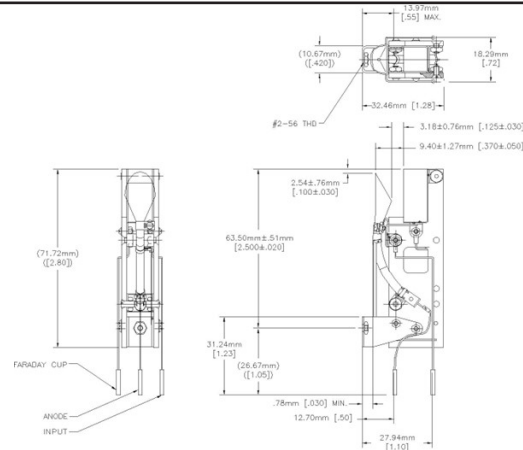
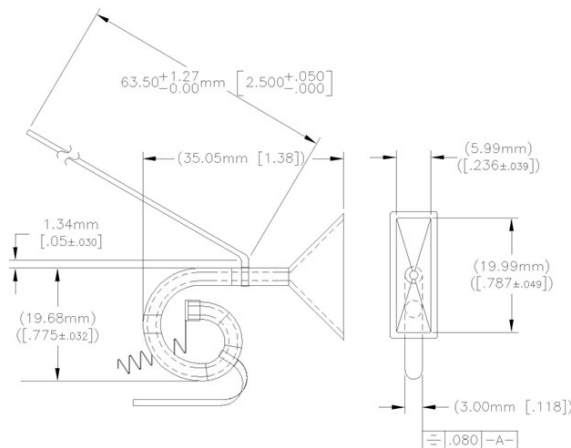
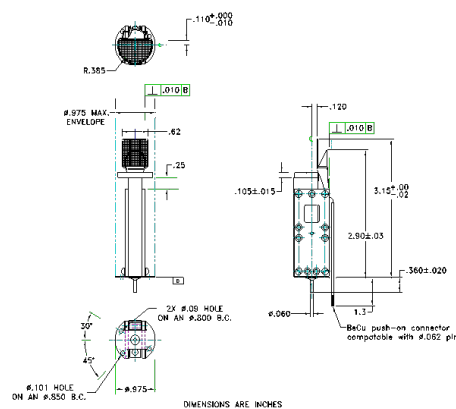


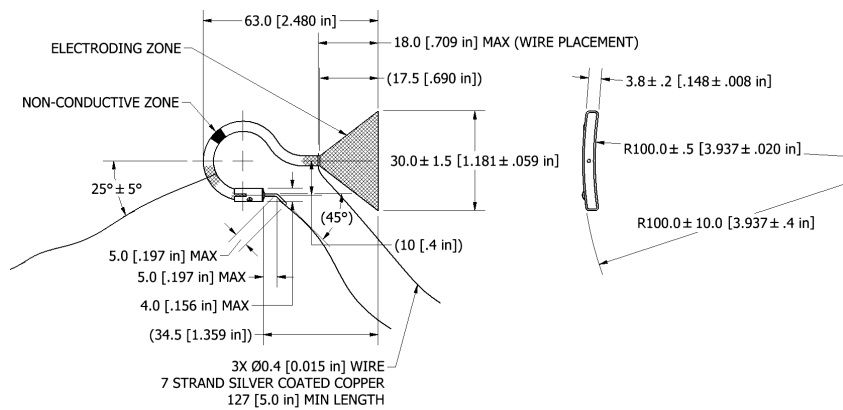
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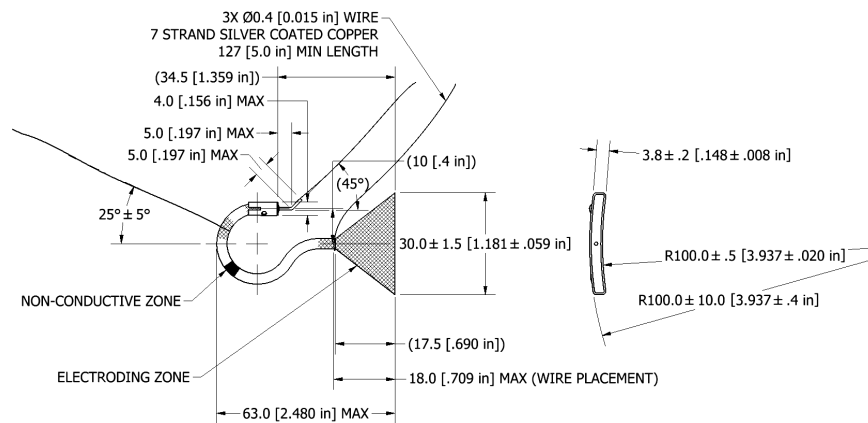
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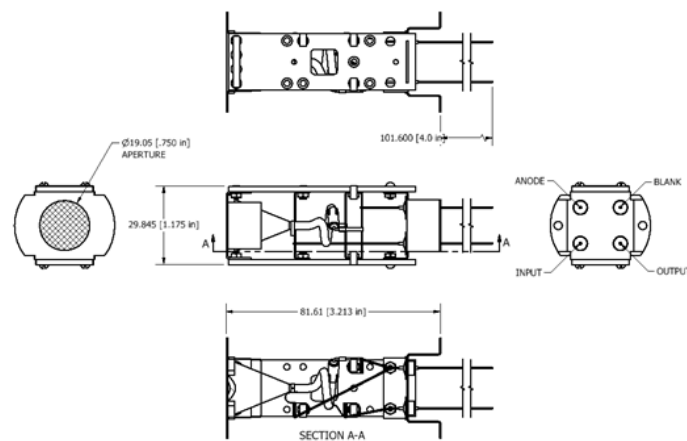

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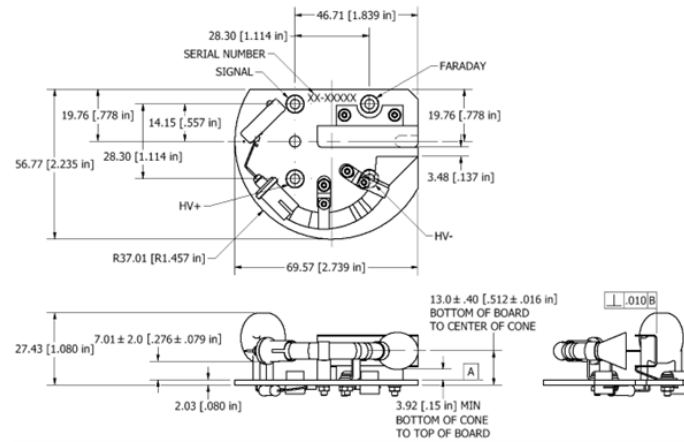
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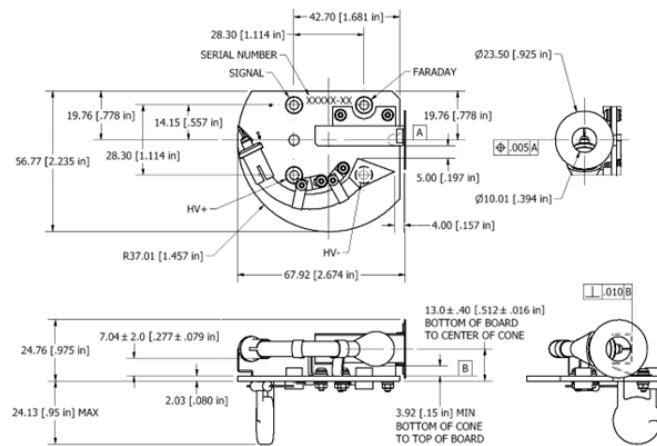
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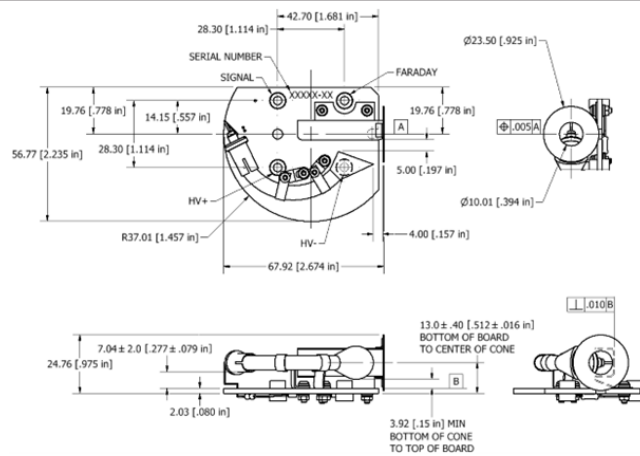
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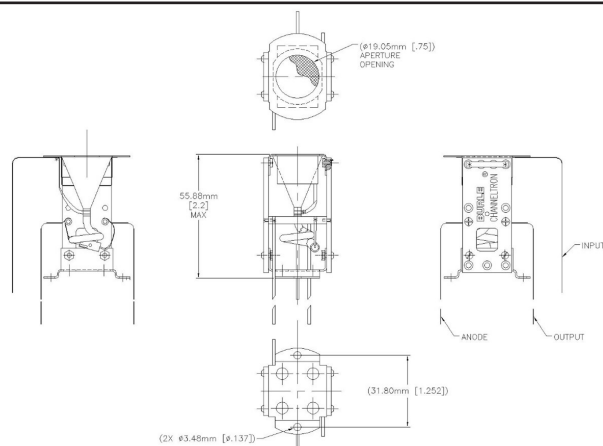
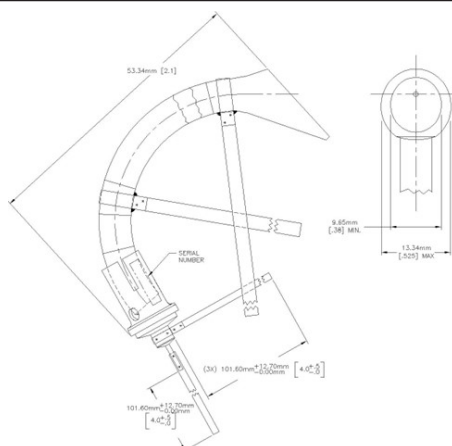
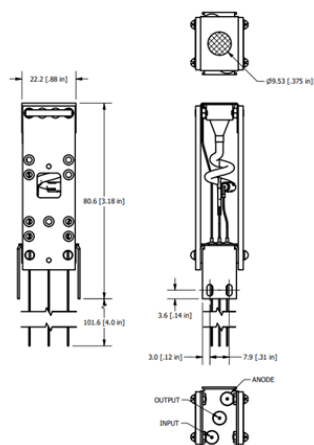
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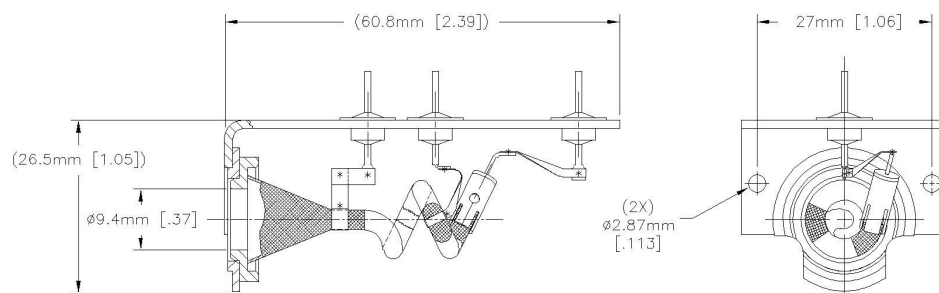


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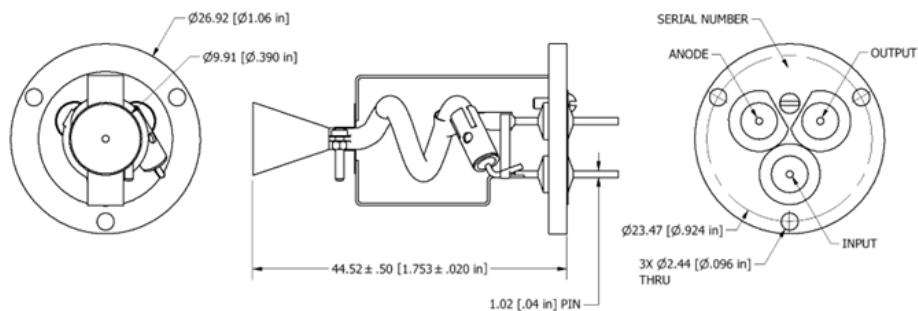


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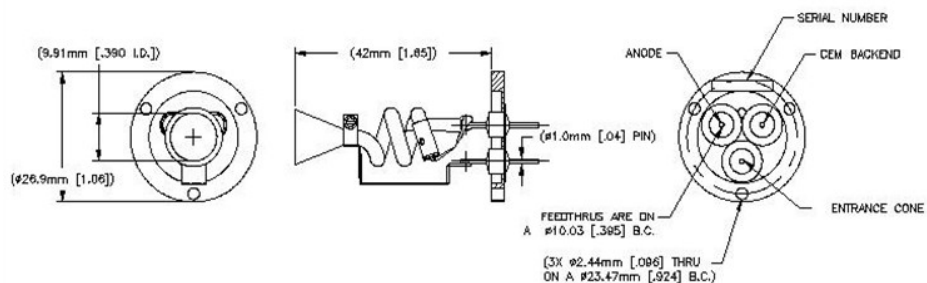

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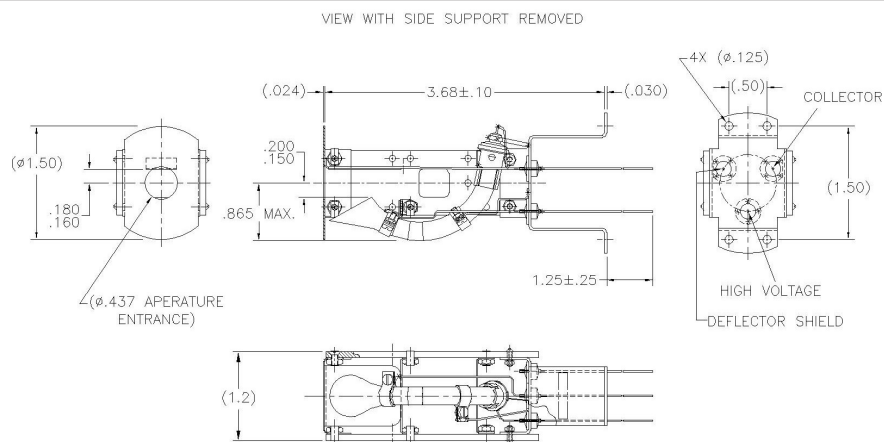
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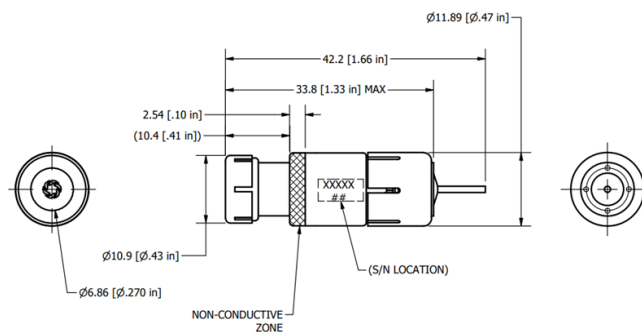
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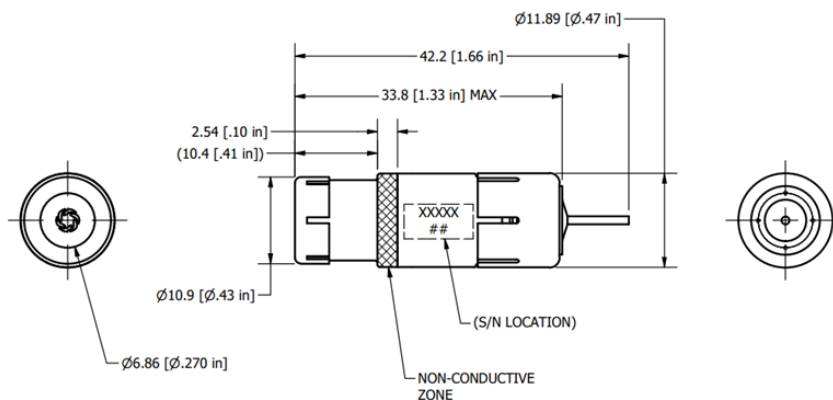
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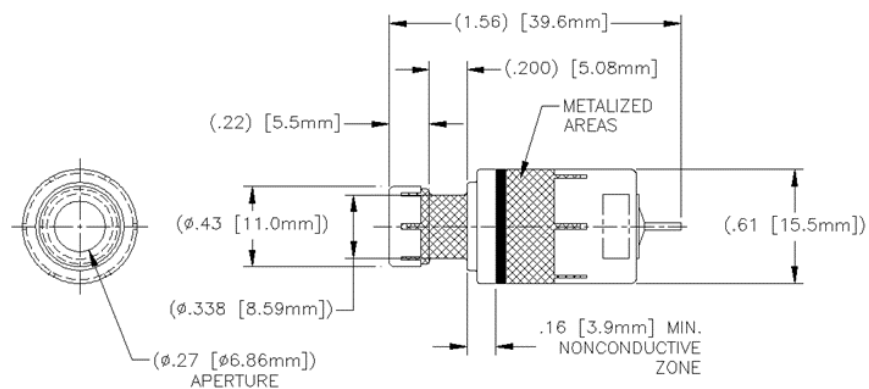
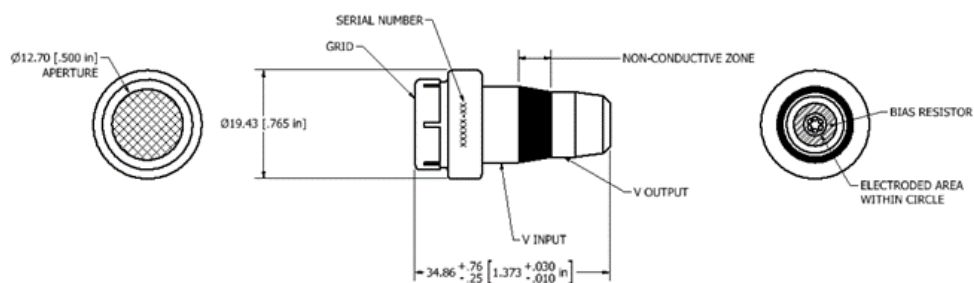
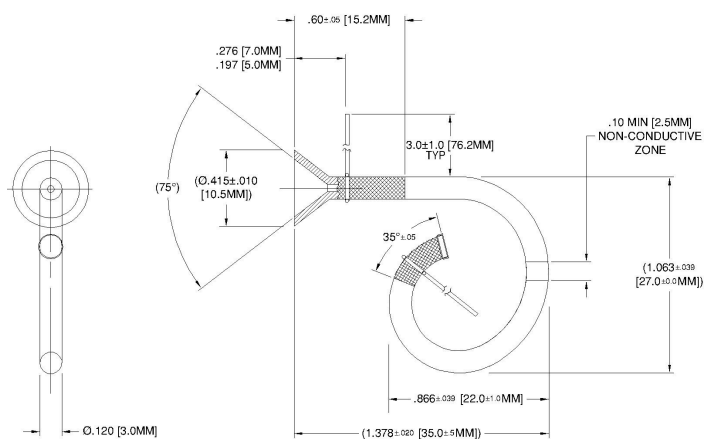
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Channeltron® 5900



Channeltron® 5901


Channeltron® 5902

Channeltron® 5903

Channeltron® 7010

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NOTES

APPENDIX A

PRODUCTION TESTING AND QUALITY ASSURANCE OF CHANNELTRON® CEMS

All Photonis Channeltron® CEMs are fully tested prior to shipment from the factory in order to assure the highest possible quality and performance in a customer's instrument. Routine CEM quality assurance procedures include both a full electrical performance test and a mechanical inspection to exacting standards.

ELECTRICAL PERFORMANCE TESTING

STANDARD PRODUCTION

Historically, all multipliers have been tested in the pulse counting mode—even those designated as analog units. This is because the test equipment required is simple and the measurements are straightforward. Figure A-1 shows a schematic of the standard CEM test configuration. The output of the CEM is fed into a charge sensitive preamplifier and subsequently into a multi-channel analyzer (MCA). The MCA is a device which assigns each pulse a value based upon its total charge and displays the resultant distribution on a CRT.

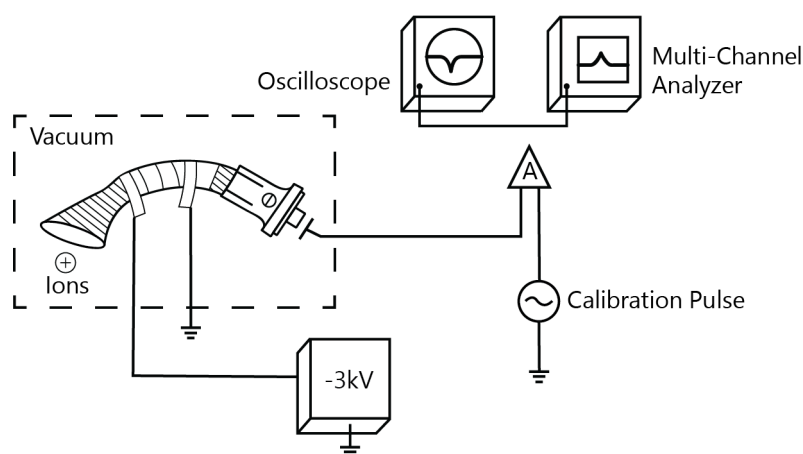


Figure A-1 Channeltron® Production Test Configuration

In addition to the CEM pulses, a calibrated voltage pulse is integrated across a capacitor of known value and also input to the MCA. The number of electrons in the calibration pulse is determined as follows:

$$N = Q/q = CV/q \text{ where:}$$

- C = the known capacitance in farads,
- V = the voltage amplitude of the calibration pulse,
- q = the charge on one electron (1.6×10^{-19} coulombs)

The CEM output pulses are compared to this known pulse value to determine the gain. CEM gain as measured in this manner is calculated by:

$$G = C_p / C_c \times N \quad \text{where,}$$

C_p = the channel number in which the peak (modal) gain occurs,

C_c = the channel number containing the calibration pulse, and

N = the number of electrons in the calibration pulse

This formula is valid for a quasi-gaussian pulse height distribution (PHD) only. For CEMs operating in the analog mode, the most probable gain (modal gain) must first be determined. This is accomplished by finding the channel where the PHD has dropped to 25% of its original value as illustrated in Figure A-3. The channel C_c , with the modal gain is then determined by:

$$C_p = C_{.25} / 1.38$$

The factor 1.38 is $-\ln(.25)$ which is a consequence of assuming the PHD to be a true negative exponential curve and that the most probable gain does occur within the first 75% of the distribution. This channel number is then related to the CEM gain via the calibration pulse as in the previous equation. In practice, this procedure produces reasonably consistent results which, if not exact, are at least correlated to measured analog gain.

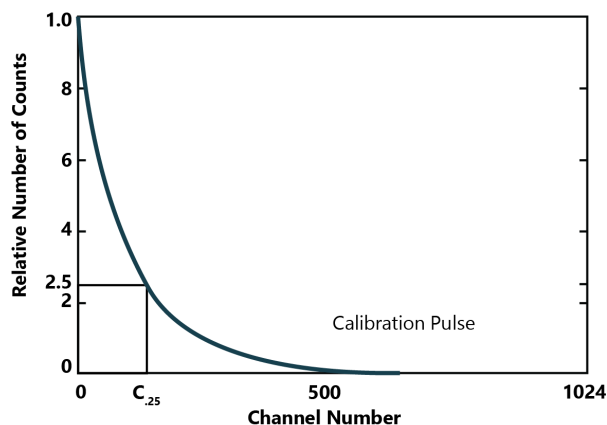


Figure A-2 Typical Analog Pulse Height Distribution

TRUE ANALOG TESTING OF CEMS

Since most mass spectrometry applications require CEMs to be operated in the analog mode, it is essential that true analog measurements be made on occasion in order to fully characterize the performance of new detector models and to periodically check standard units and test procedures for accuracy. Galileo has developed a method and facility for accomplishing this process which is illustrated schematically in Figure A-4. The source is a low current ion gun capable of producing beams of elec-

trons or positive inert gas ions. The input current (I_i) is measured in a standard Faraday cup. The beam is then deflected into the entrance aperture of the CEM and the output current (I_o) is measured. Analog gain then is calculated simply as follows:

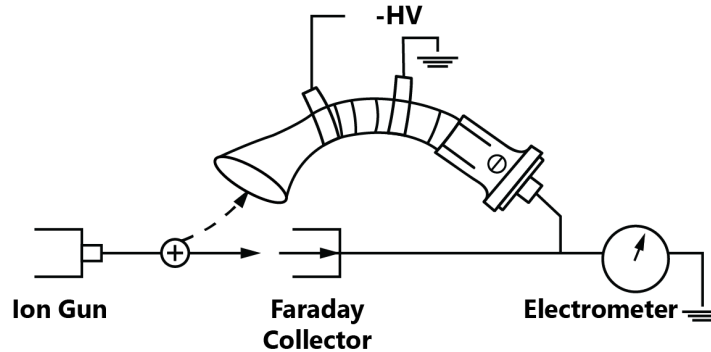


Figure A-3 Analog Test Configuration

$$G = I_o/I_i$$

MECHANICAL INSPECTION

Mechanical inspection occurs formally at two stages: 1) incoming parts are inspected prior to delivery to the shop floor and 2) after assembly, each unit is checked to ensure conformity to the latest manufacturing drawings. In addition, all spot welds and other connections are checked for mechanical integrity (see Figure A-5). In addition to these formal steps, each assembler carefully inspects his or her work prior to passing it on to the next work station.



Figure A-4 Mechanical Inspection Bench

APPENDIX B

GLOSSARY OF TERMS

Analog

Pertains to the measurement of CEM output current as a continuously variable quantity; as with a meter or linear amplifier. The analog mode may also be referred to as the current measurement mode.

Anode

The collector electrode of a CEM detector. The anode is the most positive electrode in the CEM circuit.

Bakeable

The ability of a CEM to withstand a vacuum bake procedure. Most CEMs used in mass spectrometry are capable of being baked (with no voltage applied) at 350 °C unless otherwise specified.

Bias Current

The DC current flowing in the walls of the CEM and driven by the power supply. Bias Current was formerly called "strip current."

Burn-in

The operation of CEMs prior to their ultimate application in order to stabilize their characteristics and identify premature failures. Burn-in is sometimes also referred to as "preconditioning."

Collection Efficiency

A measure of the ability of a CEM to collect the available signal. Collection efficiency is a function of such parameters as CEM cone geometry, and the presence and potential of nearby electrodes. Collection efficiency should not be confused with detection efficiency.

Conversion Dynode

An electrode (usually metal) used for accelerating ions exiting a mass analyzer to a high velocity in order to enhance detection efficiency. This is accomplished by holding the conversion dynode at a high potential opposite to the charge of the incoming particle. Typical conversion dynode potentials range from $\pm 3\text{kV}$ to $\pm 10\text{kV}$. Ions striking the conversion dynode produce many secondary particles which are in turn detected by the CEM.

Dark Count Rate

The CEM output count rate in the absence of an input. Dark count rate is a pulse counting measurement and is usually given in counts per second (cps).

Dark Current

CEM output current in the absence of an input. Dark current is an analog measurement and may be affected by elements outside the CEM proper, such as leakage current in the collector assembly.

Detection Efficiency

The ability of an incident particle to induce secondary electrons in a CEM. The detection efficiency of a CEM is strongly dependent upon parameters such as the mass-to-charge ratio, velocity, and momentum of incident particles. Detection efficiency should not be confused with collection efficiency.

Dynamic Range

The ratio of maximum to minimum detectable signals. For analog CEMs, dynamic range is a function of dark current and maximum linear output current. For pulse counting CEMs, dynamic range is a function of dark count rate and maximum output count rate capability.

Full Width at Half-Maximum (FWHM)

A figure of merit for the output pulse height distribution (PHD) of CEMs operated in the pulse counting mode. The FWHM is a measure of the narrowness of the quasi-gaussian PHD produced by saturated CEM output pulses. It is usually expressed as a percent and calculated by dividing the peak or modal gain value by the gain range at half the peak height, and multiplying the result by 100% (see Figure 2-8).

Gain

The ratio of the amplitude of the output signal to the amplitude of the input signal. Analog and pulse counting gain measurements are made via different procedures, however, the result can still be considered the ratio of output to input signals.

Gain Stability

A measure of the uniformity of CEM gain over time. A CEM is considered to exhibit gain stability if measured gain values taken at 1.6mC intervals of output charge deviate by less than $\pm 3\%$.

Lifetime

The limit beyond which useful signal can no longer be obtained at an applied voltage of 3kv. Lifetime can be expressed either as a measure of total accumulated output charge or in hours of operation under stated conditions of pressure, gain, and input. Lifetime is very strongly dependent on ambient conditions during operation but is typically about one year in most mass spectrometry applications, assuming operation of approximately 40 hours per week.

Linearity

The ability of a CEM to produce an output current which varies directly and linearly (in a

straight line function) with respect to the input. Most analog CEMs will produce linear output currents of up to 10-15mA.

Mass Discrimination

The property of a CEM by which the gain varies as a function of the mass of incident ions. In general, the higher the mass, the lower the gain (detection efficiency) for constant energy ions.

Microphonics

The noise signal induced in the output (or collector) circuit of a CEM by coupling due to mechanical vibration of nearby circuit elements or sources.

Plateau

That portion of the count rate versus voltage characteristic over which the count rate is substantially independent of the applied voltage.

Pulse Counting

A non-linear CEM operational mode for which all output pulses are nearly the same amplitude due to space charge saturation. Pulse counting is used in digital systems and when detecting extremely low level input signals.

Pulse Height Distribution (PHD)

The distribution of the amplitude of CEM output pulses for a given applied voltage. Pulse counting CEMs produce a quasi-gaussian PHD at gains in excess of about 5×10^7 while the PHD of analog CEMs is essentially a negative exponential.

Pulse Width

The time interval between the first and last points at which the instantaneous amplitude of a CEM output pulse reaches 90% of its peak value. For most CEMs, the pulse width is about 20ns.

Rise Time

The time interval for the leading edge of a CEM output pulse to move from 10% to 90% of its peak amplitude. The rise time for typical CEM output pulse is about 3-5ns.

Signal-to-Noise Ratio (S/N)

The ratio of the value of the signal amplitude to that of the noise. S/N is a measure of the noise added by the detector. Typical noise levels for CEMs are:

Analog Dark Current — $< 1\text{pA}$ at a gain of 10^6

Dark Count Rate — $< .05\text{cps}$ at a gain of 10^8

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